Mechanics and Thermodynamics of Mixtures with Continuous Diversity

From Complex Media to Ice Sheets

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To my dear Gis

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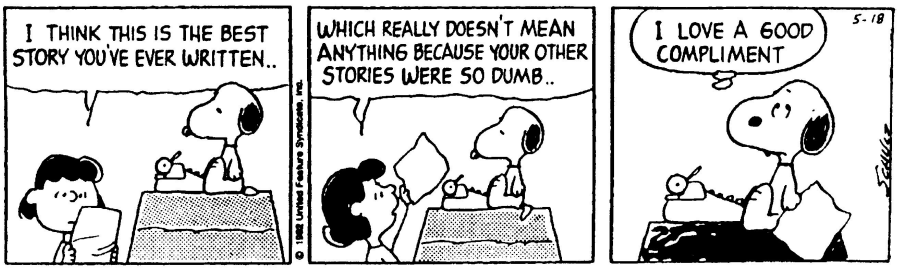


Abstract

The aim of this thesis is to introduce to the reader the thermodynamic theory of mixtures with continuous diversity and to illustrate its potential through applications to diverse complex media.

Chapter 1 offers a critical discussion about the intricacies in the description of complex media as continuous bodies. Fundamentals on the homogenization (structural averaging) of porous materials are presented in a concise way.

Chapter 2 gives an up-to-date review of the homogenization of polar granular media, with emphasis on the peculiarities of its microstructure.

Chapter 3 combines the concepts of homogenization, polar media and chemical mixtures in a systematic manner, in order to derive appropriate balance equations for mixtures of microstructured media.

Chapter 4 invokes the results of former chapters to resolve a contemporary polemic concerning energy invariance and inertial effects in chemically reacting mixtures of liquid crystals.

Chapter 5 introduces the fundamental concepts of the thermodynamic theory of mixtures with continuous diversity from a generic perspective.

Chapter 6 merges the formerly presented notions of microstructured media, chemically reacting mixtures and mixtures with continuous diversity into the powerful theory of hybrid mixtures with continuous diversity, or "doubly complex" media.

Chapter 7 employs the theory of mixtures with continuous diversity to study the microstructure evolution of polymeric solutions, more precisely suspensions of rigid rodlike macromolecules.

Chapter 8 demonstrates how the texture evolution of polycrystalline media undergoing recrystallization may be modeled by using the formalism of mixtures with continuous diversity. Besides a short historical synopsis of ice morphology research, the particular case of induced anisotropy and recrystallization in ice sheets is considered.

Chapter 9 concludes this work with an overview on future applications, specially on the modeling of iceberg ensemble dynamics during Heinrich events, as well as on the study of abrasion, fragmentation and particle size segregation in polydisperse granular media.

The most significative results of this dissertation comprehend:

1. the clarification of the similarities between homogenization (structural averaging) of microstructured media and the continuum description of chemical mixtures;
2. the solution of Müller's paradox of frame dependence in chemically reacting mixtures of liquid crystals;
3. the thermodynamic theory of mixtures with continuous diversity;

4. the derivation of balance equations and jump conditions for chemically reacting mixtures of microstructured media;
5. the development of a constitutive theory for polymeric solutions of rodlike macromolecules within the frames of the theory of mixtures with continuous diversity;
6. the construction of a thermodynamically consistent continuum theory for creep and recrystallization of ice sheets;
7. the outline of a description of abrasion and fragmentation from the viewpoint of mixtures with continuous diversity.

Zusammenfassung

Das Ziel dieser Doktorarbeit ist die Einführung einer thermodynamischen Theorie für Mischungen mit stetiger Diversität und ihr Potenzial durch Anwendungen für verschieden komplexe Medien zu veranschaulichen.

Kapitel 1 ist eine kritische Darstellung über die Schwierigkeiten bei der Beschreibung komplexer Medien als Kontinua. Grundlagen über Homogenisierung (structural averaging) von poröse Materialen werden anschaulich präsentiert.

Kapitel 2 gibt einen aktuellen Überblick über die Homogenisierung polarer granularer Medien, mit besonderer Betonung der Eigenheiten der Mikrostruktur.

Kapitel 3 kombiniert die Begriffe der Homogenisierung, der polaren Medien und der chemischen Mischungen in systematischer Weise, um die passenden Bilanzgleichungen für Mischungen von mikrostrukturierten Medien herzuleiten.

Kapitel 4 nutzt die bisherigen Ergebnissen, um eine aktuelles Problem über Energieinvarianz und Trägheitseffekte in chemisch reagierenden Mischungen von Flüssigkristallen zu lösen.

Kapitel 5 führt die allgemeinen Grundlagen der Thermodynamik von Mischungen mit stetiger Diversität ein.

Kapitel 6 führt nun die vorher präsentierten Begriffe der Medien mit Mikrostruktur, der chemisch reagierende Mischungen und der Mischungen mit stetiger Diversität zusammen, um die Theorie von hybriden Mischungen mit stetiger Diversität, oder doppelkomplexer Medien, herzuleiten.

Kapitel 7 benutzt die Theorie der Mischungen mit stetiger Diversität für die Untersuchung der Mikrostrukturentwicklung von Polymerlösungen fester, stabförmiger Makromoleküle.

Kapitel 8 zeigt, wie die Texturentwicklung von rekristallisierenden Polykristallen durch die Theorie der Mischungen mit stetiger Diversität modelliert werden kann. Ausser einer kurzen, historischen Übersicht über die Eismorphologieforschung wird der Sonderfall der induzierten Anisotropie und Rekristallisation in Eisschilden dargestellt.

Kapitel 9 schliesst die Arbeit mit einer Überblick über künftige Anwendungen, insbesondere die Modellierung der Dynamik von Eisbergen während sogenannter "Heinrich-Events", sowie der Forschung über Abrasion, Fragmentierung und Teilchengrößetrennung in polydispersen Granulaten.

Die Hauptergebnisse dieser Arbeit sind:

1. Darstellung der Ähnlichkeiten zwischen Homogenisierung mikrostrukturierter Medien und der Kontinuumsdarstellung chemischer Mischungen;
2. Lösung des Müller-Paradoxons (Bezugssystemabhängigkeit der inneren Energie in chemisch reagierenden Mischungen von Flüssigkristallen);
3. Die thermodynamische Theorie der Mischungen mit stetiger Diversität;

4. Herleitung der Bilanzgleichungen und der Sprungbedingungen für chemisch reagierende Mischungen von Medien mit Mikrostruktur;
5. Entwicklung einer konstitutiven Theorie für Polymerlösungen fester, stabförmiger Makromoleküle im Rahmen der Mischungstheorie mit stetiger Diversität;
6. Bildung einer termodynamisch konsistenten Kontinuumstheorie für Kriechen und Rekristalisation von Eisschilden;
7. Entwurf einer Darstelung von Abrasion und Fragmentierung aus Sicht der Mischungstheorie mit stetiger Diversität.

Contents

Part I

Prosaic View of Heterogeneous and Microstructured Media

Facing the Frightening Beasts of Continuum Theory

1. When the Discrete Resolves into a Continuous

Die große Aufgabe, welche seit der Pythagoreischen Entdeckung des Irrationalen gestellt ist, das uns (namentlich in der fließenden Zeit und der Bewegung) unmittelbar anschaulich gegebene Stetige *nach seinem in „exakten" Erkenntnissen formulierbaren Gehalt als Gesamtheit diskreter „Stadien" mathematisch zu erfassen, dieses Problem ist trotz Dedekind, Cantor und Weierstrass heute so ungelöst wie je.*

Hermann Weyl, [426] p. 16

By definition, heterogeneous media are composed of dissimilar constituents, often non-uniformly distributed in space, in such a way that their physical and chemical properties can vary from point to point. Typical heterogeneous materials are polycrystals, granular and porous matter, chemical mixtures, suspensions and emulsions. Less orthodox examples of heterogeneous media include spatially distributed populations (of animals, bacteria, plants, etc.) and assemblages (of e.g. asteroids, icebergs, oscillators or vehicles). Clearly, most heterogeneous systems can be often regarded, on appropriate length and time scales, as aggregates of many discrete elements. Nevertheless, on considerably larger scales, it frequently happens that such systems can – under suitable circumstances – be viewed as continuous media. It is the intention of this chapter to give some insight on the most common situations under which such an upscaling can be carried out, as well as its possible consequences.

1.1 Motivation

In our quotidian, it is so natural to merge complex heterogeneous aggregates of discrete elements into smooth media that this often turns to be an ordinary, even spontaneous, process. For instance, the human skin is such a marvelous material whose smoothness is subject of women's greatest care, even though we must actually recognize that, on a microscopic level, it consists of a rather inhomogeneous structure of many different living cells – a harsh picture to vain eyes. On the other hand, the even faces of a rock crystal are impressive macroscopic manifestations of the highly ordered packing of its discrete particles, namely silicon and oxygen atoms. In fact, for most crystals, the peculiar lattice symmetries found on the microscale are theoretically able to persist almost indefinitely over larger scales. In practice, however, huge single crystals are considerably rare in nature: it is much easier to find

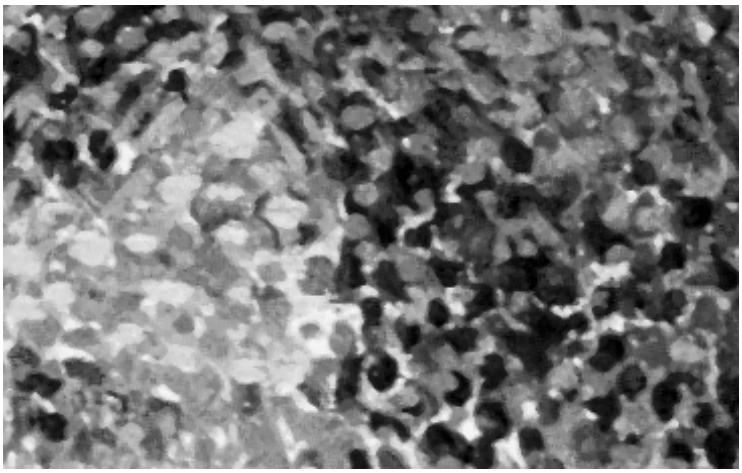


Fig. 1.1. An unidentified aggregate of colored elements. In this grayscaled version, lighter gray tones correspond to brighter hues (like yellow, orange and cyan), while darker shades of gray to colors like red, royal blue and dark green

crystalline matter in the form of heterogeneous aggregates of smaller crystallites, the so-called *polycrystals*.

Of course, heterogeneity is not exclusively found on the microscale. In fact, even on a macroscopic level we can find good examples of heterogeneous systems made of discrete components whose distinctive properties induce astonishing features on a larger scale, where the discreteness is smeared out. For instance, in Fig. 1.1 we see an aggregate of granular elements or cells, which could possibly be grains of a granular material or crystallites of a polycrystal. These cells are all more or less spherical and of similar size, but not identical, for they can be distinguished by their respective colors (with a bit of imagination, it is easy to recognize the original colors from the grayscaled picture presented in Fig. 1.1). There is no meaningful pattern, in spite of a clear segregation of darker and lighter elements (notice also the inclusion of darker cells on the bottom-left of this picture). What should this mean?

One possibility could be that Fig. 1.1 was produced by a piece of some translucid polycrystalline mineral. Indeed, by sandwiching the mineral between two crossed polarizers horizontally disposed, and further illuminating the resulting arrangement from below, an image with similar qualitative features of Fig. 1.1 emerges. In this case, the colors are produced by an interaction between the polarized light and the crystalline lattice of each crystallite. Depending on the orientation of this lattice, a different color comes out.

Another possible interpretation of Fig. 1.1 might be a photomicrography of a granular material, for instance some kind of artisanal work made with different types of sand. In fact, sand drawings are traditional in various cultures, as illustrated in Fig. 1.2, a work made by a member of a fishermen community of Northeastern Brazil. According to the artisan, the technique is basically to fill the bottle gently, layer by layer, with different types of sand, chosen according to the desired color for the given layer. It should be observed that, by finishing, the artisan must carefully seal the bottle in a hermetic manner, in order to avoid particle segregation by shaking, which could destroy the whole figure.

(a) **(b)**

Fig. 1.2. Artisanal work of art. **(a)** Small bottle filled with distinct colored types of sand. **(b)** Detailed view, evidencing the individual sand grains. From the coast of Ceará, Brazil

Diverse other conjectures about Fig. 1.1 could be proposed, but further digression would bring no progress, for it is clear that more information is still required. This can be obtained by analyzing the system at hand from a larger perspective, as shown in Fig. 1.3. From this upscaled picture it becomes evident that the "unidentified aggregate" is in fact a detail of a work of art, namely a painting, entitled *Circus Sideshow*. It was made at the end of 19$^{\text{th}}$ century by the French painter Georges-Pierre Seurat, using a neo-impressionist technique which became known as *pointillism* (or *divisionism*[1]). Seurat's intention was to produce more vivid and "realistic" hues by exploiting the interaction between tiny detached brushstrokes of contrasting colors, which should blend together when looking at the entire work (Fig. 1.4). He knew that such color interactions were very intricate, compelling a skilled artist to have a deep knowledge of its physics. Therefore he studied along his short life numerous influential treatises on the subject, from Blanc [45] and Chevreul [74] to Maxwell [294, 295] and Helmholtz [205], rendering him to be considered by many "the ultimate example of the artist as scientist" [288].

[1] It should be remarked that Seurat himself had preferred to call his technique *chromoluminarism* [288]. The terms "pointillism" and "divisionism" seem to have come in trend after his death.

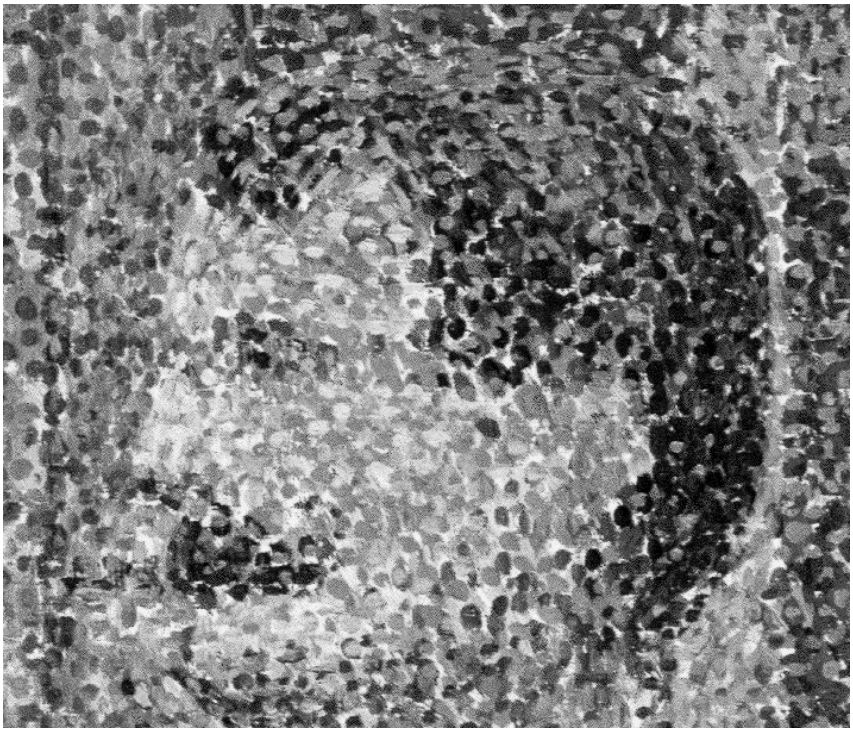


Fig. 1.3. Larger view of the unidentified aggregate of colored elements, enclosing the region already shown in Fig. 1.1

Fig. 1.4. *Circus Sideshow* (1887-88), by G.-P. Seurat. Oil on canvas, 99.7×149.9 cm. In exposition at the Metropolitan Museum of Art, New York (bequest of S. C. Clark, 1960, URL: `www.metmuseum.org`)

By comparing Figs. 1.1 and 1.4, it is quite impressive to see how the "granular" features of Seurat's paintings become smoothened on a larger scale. Quoting Schapiro [373]:

> "*... the continuous form is built up from the discrete, and the solid masses emerge from an endless scattering of fine points...*" (p. 101)

From the discussion above, there must be recognized the crucial role played by the distinguishing features of the elements of a given aggregate, as well as the way these elements interact. For instance, tiny brushstrokes are basic elements in the pointillism, and these are distinguished according to their particular colors. Nevertheless, the interaction of blue and violet strokes in a painting is strongly dependent on the amount of yellow, orange or green in their surroundings. Moreover, hue and saturation on the large scale can be quite different from those observed on the discrete, "granular" level. Consequently, depending on the choices for characterization and interaction of the basic constituents of the medium, a rather different large scale reality can emerge.

1.2 Homogenization and the Continuum Hypothesis

Attention was devoted in the last section to a special sort of medium, viz. one whose discrete elements are distinguished by their colors. This served not only to illustrate how frequent and spontaneous are smearing processes in nature (remember in passing that almost all pictures and images in our modern quotidian are composed of minute points and pixels – like a photograph or a video screen) but also to demonstrate the sensibility of the averaging process on the assumed interactions and distinguishing properties of the basic constituents. As a consequence, the character of the emerging continuum is strongly dependent on the relevant features and interactions of its discrete elements.

At this point, however, a crucial question naturally arises: how can one express formally such an intuitive transition from discrete to continuous? Even though many specialists on continuum mechanics might say that this is a trivial task, it is generally not. The motive for such an awkwardness is basically the *metaphorical character* of many fundamental concepts of continuum mechanics, specially when applied to heterogeneous and microstructured media. This is indeed one reason why such continua have been also subsumed together under the abstruse term "*complex media*".

Historically, the most essential concept of continuum physics – the so-called *continuum hypothesis* – has been formulated based on our ordinary experience with "simple" media like water and air, as didactically explained in the celebrated treatise by Batchelor [26]:

> "*We shall suppose,* [...]*, that the macroscopic behavior of fluids*[2] *is the same as if they were perfectly continuous in structure; and physical quantities such as*

[2] Although this statement refers only to fluids, similar arguments have been also adopted to simple solids (see e.g. [153]).

> *the mass and momentum associated with the matter contained within a given small volume will be regarded as being spread uniformly over that volume instead of, as in strict reality, being concentrated in a small fraction of it. The validity of the simpler aspects of this* continuum hypothesis *under the conditions of everyday experience is evident. Indeed the structure and properties of air and water are so obviously continuous and smoothly-varying, when observed with any of the usual measuring devices, that no different hypothesis would seem natural.*" (pp. 4 and 5)

It must be emphasized that the notion of "*perfectly continuous*" quoted above is in fact figurative. It is related to the mathematical (and also metaphorical) concept of continuity as applied to calculus, in contrast to the more intuitive notion of *natural continuity* derived from our most instinctive idea of motion, space and time. As defined by Lakoff & Núñez [256]:

Definition 1.2.1 (Naturally Continuous Space [256]). *Space is absolutely continuous. Space does not consist of objects. Rather, it is the background setting that objects are located* in. *Space exists independently of, and prior to, any objects located in space. Planes, too, are absolutely continuous. They, too, are not made up of objects but have location on them where objects can be situated. Similarly, a line or curve is absolutely continuous, like the path traced by a moving point. Lines and planes also exist independently of, and prior to, any objects located on them.*

Points are locations in space, on lines, or on planes. They are not objects that can exist independently of the line, plane, or space where they are located. Dimensionality is a property of a space, a plane, or a line.

A similar conception of naturally continuous space, with emphasis on its independence of the material objects located in it, can be found also in the work of Maxwell [299], in connection with the notion of *absolute space*.

By comparing Def. 1.2.1 with the continuum hypothesis already quoted, the metaphorical content of the latter becomes evident. For instance, points in a continuum are not really points in the natural sense defined above, since they shall contain matter *within* them. The matter enclosed in one of these "points" (which are actually better seeing as small volumes) constitutes what is sometimes called a *material point* (or *particle*) and it is characterized by the same properties as the medium itself. Precisely at this moment, the distinction between "simple" and "complex" media becomes discernible: in contrast to "simple" media, the matter contained within a given small volume of an heterogeneous or microstructured medium cannot be straightforwardly regarded as being spread uniformly over that volume, seeing that – in such "complex"media – matter is not only characterized by its mass but also by other intrinsic properties, like porosity, chemical composition (expressed by the mass fractions of its constituents), polarization and texture (described by directors and structure tensors).

Special methods of averaging over small volumes must therefore be employed, in order to adapt the preservation of the intrinsic properties of heterogeneous and

microstructured media to the basic requirement of "mass being uniformly spread over small volumes" imposed by the continuum hypothesis. Such averaging procedures – often also called *homogenization*[3] methods – shall partially or fully accomplish the transition from discrete to continuum, illustrated in the last section. Actually, there are in the literature diverse homogenization approaches available to this end, from the most instinctive to some extremely involved, depending on the characteristics of the medium and the scale of the problem. Some of them will be discussed afterwards.

Finally, there must be emphasized the importance of keeping in mind the metaphorical sense of continuum, when working with heterogeneous and microstructured media. Even veteran specialists on continuum physics have occasionally been driven to mistaken conclusions when working with heterogeneous and microstructured media, simply because they forgot – just for a moment – to think using the metaphor of continuum and employed the natural continuum concept instead. Two recent examples of such a situation will be reviewed later on (see Footnote 8 in Sect. 3.5 and Sect. 4.2). Indeed, it takes special training to think in terms of the metaphor of a continuum, and it must be borne in mind that even specialists on the subject do not use such a metaphor in their everyday lives or when they are talking to non-specialists. As provocatively asserted by Lakoff & Núñez [256]:

> "*Is the Continuum hypothesis about the continuum? It is certainly about the real numbers. It is not about the naturally continuous line. For those people who believe that the term "the continuum" refers to the naturally continuous line, the Continuum hypothesis is not about the continuum.*
> *There is nothing strange or paradoxical or wondrous about this. It is simply a matter of being clear about what you mean.*" (p. 290)

1.3 The Homogenization Wonder: Porous, yet Continuous!

In order to fix the ideas presented so far, it is opportune now to examine some elementary features of common homogenization processes.

Returning to Fig. 1.2, it can easily be recognized (e.g., by simple visual examination of the picture) that the compacted sand within the photographed bottle has an evident porous texture, similar to that of ceramics or sedimentary rocks. Actually, pores (and interstices) are natural features of countless materials and tissues found everywhere: skin of animals, bones, epi- and/or peridermis of plants, soil, snow and firn, most types of wood, clothes, bread and cookies, plastic and metallic foams, ceramics and many rocks, among others.

In spite of this ubiquitousness – or must probably because of it – the precise definition of porous medium is not a facile task. Initially, with a view to distinguish pores

[3]The term "homogenization" – as used in materials science and continuum physics to describe processes of upscaling and averaging – is somewhat ambiguous and should not be misinterpreted: it does *not* mean that the medium acquires a homogeneous, uniform character throughout. Actually, the continuum usually remains *heterogeneous* after the process of averaging. The homogeneity is accomplished only on a microscale, i.e., within a "point" of the continuum (material particle), whereas the (chemical) constitution and properties of the medium still can vary in time and diverge from point to point.

from bubbles, the voids within the material should be required to be interconnected, forming so ordered or random meshes of channels throughout the medium. However, a naive definition of porous material as "a solid with holes" obviously does not fit, for it would not exclude hollow cylinders, framed structures, etc. Consequently, it transpires that an appropriate definition of porous medium have to be relative (i.e., scale dependent), in order to ensure the existence of pores instead of large orifices, so that the sizes of the "holes" shall be much smaller than the characteristic dimensions of the problem. So, after Bear [30] and de Boer & Ehlers [47] the following definition of porous material is put forward *without pretension of absolute generality*:

Definition 1.3.1 (Porous Medium). *A portion of space occupied by heterogeneous (multiphase) matter is considered a* porous medium *if the following conditions are satisfied* in every "point" of the continuum*:*

① *One phase is solid. It is named the* solid matrix *and cannot be absent. It might not be a single constituent phase, but rather a mixture of distinct solid materials (as, e.g., in soil). In the latter case, the solid matrix comprises all solid constituents together. The part of the medium which is not occupied by the solid matrix is denominated the* void (*or* pore *or* interstitial) space.

② *At least one phase is* not *solid. It may be gaseous, liquid or absent (vacuum). The gaseous and liquid phases constitute the* interstitial fluid(s). *A porous medium is called* saturated *if its whole pore space is filled with interstitial fluids, and* unsaturated *otherwise. In particular, if its void space is empty (i.e., no interstitial fluid present) the porous medium is called* dry.

③ *The sizes of the various openings comprising the void space must be sensibly smaller than the characteristic dimensions of the problem, or in other words, the interstices must be* sufficiently narrow. *At least some of the pores of the void space should be interconnected; these constitute the* effective pore space.

It must be emphasized that the above definition might be limited, but it suffices for understanding the basic features of porous media within the present scope.

In the light of Sect. 1.1, the foregoing reasoning would already yield sufficient grounds to justify the need for a continuum approach to porous media via homogenization. Notwithstanding, there is an additional, decisive reason for choosing such an approach: the determination of the geometry of the solid surfaces, which act as boundaries for the flow of the interstitial fluid(s) in the void space, generally is a formidable problem – a genuine Gordian knot, which can nevertheless be cut by treating the porous medium as a continuum.

Available techniques to accomplish the desired homogenization include variational and renormalization methods [4, 338], asymptotic expansions [312, 337], effective medium models [142] and structural averaging approaches [30, 31, 174], among others (for a longer discussion, see e.g. [338]). The later approach is adopted here, owing to its relative simplicity, robustness and intuitive basis. Structural averaging is grounded on the notion of a *representative elementary volume* – REV (sometimes also called *representative volume element* – RVE or simply *control volume*), over

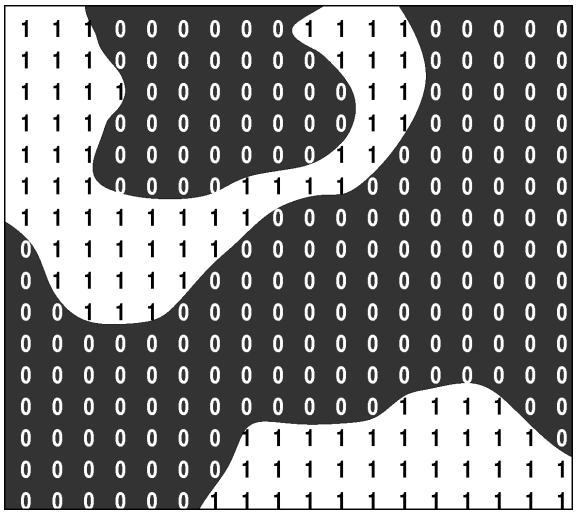


Fig. 1.5. Two-dimensional sketch of a porous medium on the microscale. The solid matrix is represented dark, while voids are white. The superposed numbers indicate the values of the voidage distribution $n_{\mathtt{D}}$ in many points $\boldsymbol{r} \in \mathcal{R}$, for this particular case

which spatial (and eventually also temporal) averages of the microscale properties of the medium are performed [31, 174, 200, 258, 427]. Consequently, the aptitude to construct a continuum theory via structural averaging depends necessarily on the existence of such a REV, i.e., on the possibility of finding an appropriate volume (valid for all points of the continuum) in which averaged quantities reproduce their experimentally observed values.

For porous matter, the most relevant of these microscale properties is of course the *porosity*[4] (or "void density") n. It represents a measure of the void space within a prescribed volume and is generically defined (i.e., on any level of description in which voids can be clearly distinguished from solid matrix) by

$$n\,(\mathcal{R},t) = \frac{1}{V_{\mathcal{R}}} \int\limits_{\mathcal{R}} n_{\mathtt{D}}\,\mathrm{d}^3 r\ , \tag{1.1}$$

where $V_{\mathcal{R}}$ represents the volume of a region $\mathcal{R}$ of space ($\mathcal{R} \subset \mathbb{R}^3$). Points inside the region $\mathcal{R}$ are specified by the *microscale position* $\boldsymbol{r} \in \mathcal{R}$, so that $\mathrm{d}^3 r$ represents a *microscale volume element*, while the center of mass of the material contained in $\mathcal{R}$ at time instant t is designated by the particular position $\boldsymbol{r} = \boldsymbol{x}$. Further, $n_{\mathtt{D}}$ stands for the *voidage distribution*, which for given time instant t can be written as (see Fig. 1.5)

$$n_{\mathtt{D}}(\boldsymbol{r},t) = \begin{cases} 1 & \text{for } \boldsymbol{r} \text{ within a void,} \\ 0 & \text{otherwise.} \end{cases} \tag{1.2}$$

The quantity complementary to porosity is the *solid volume fraction* ν, which can be defined in a similar way as

$$\nu\,(\mathcal{R},t) = \frac{1}{V_{\mathcal{R}}} \int\limits_{\mathcal{R}} \nu_{\mathtt{D}}\,\mathrm{d}^3 r\ , \tag{1.3}$$

[4] According to de Boer & Ehlers [47], the concept of porosity was introduced in 1925 by Terzaghi [400] (for a historical synopsis of the theory of porous media, see Ehlers [116] and de Boer [91]). Pioneers of the modern theory of porous media are undoubtedly Darcy [90], Fillunger [139, 140], Biot [40–42] and Terzaghi [400, 401].

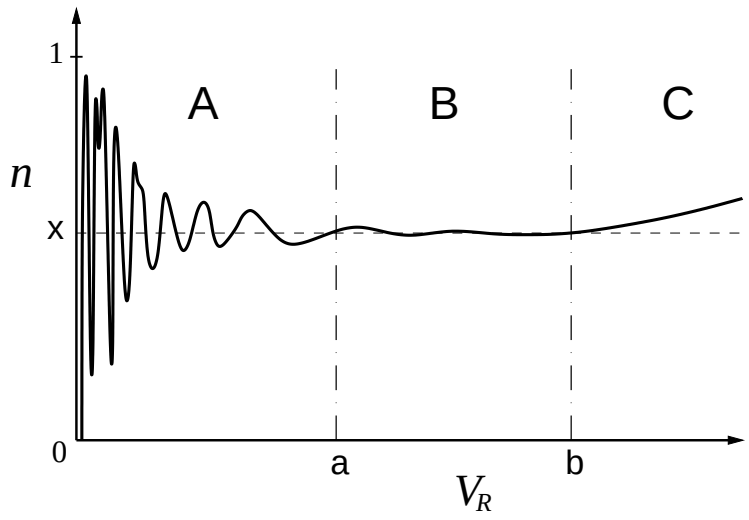


Fig. 1.6. Variation of porosity $n(\mathcal{R}, t)$ as function of the representative elementary volume $V_{\mathcal{R}}$. Sector A: domain of strong localized fluctuations. Sector B: range of values of $V_{\mathcal{R}}$ for which homogenization is possible. Sector C: domain of prohibitively large values of $V_{\mathcal{R}}$, which subsume large-scale spatial changes of porosity (i.e., macroscale inhomogeneities), yielding false estimations. The points a and b denote the recommended extrema for $V_{\mathcal{R}}$, while x marks the porosity value calculated by homogenization

with $\nu_{\mathtt{D}}$ denoting the *solid phase distribution*, viz.

$$\nu_{\mathtt{D}}(\boldsymbol{r}, t) = \begin{cases} 1 & \text{for } \boldsymbol{r} \text{ within the solid matrix,} \\ 0 & \text{otherwise.} \end{cases} \tag{1.4}$$

Of course, owing to Def. 1.3.1, there hold the identities

$$\nu = 1 - n \ , \qquad \nu_{\mathtt{D}} = 1 - n_{\mathtt{D}} \ . \tag{1.5}$$

Evidently, the quantities n and ν should generally depend not only on the position of the region $\mathcal{R}$ but also on its size and geometry. In other words, the volume integrals in (1.1) and (1.3) may usually manifest strong oscillations even for slight variations of the volume $V_{\mathcal{R}}$ or the form of $\mathcal{R}$. That is why the porosity (1.1) and solid volume fraction (1.3) are written as functions of $\mathcal{R}$ and t, instead of simply $\boldsymbol{x}$ and t. Nevertheless, it is the conjecture of the structural averaging method that *there exists a suitable volume $V_{\mathcal{R}}$ – called representative elementary volume* (REV)*, which is large enough to minimize undesirable oscillations but still so small in comparison with the characteristic lengths of the problem as to allow the construction of a field theory* (Fig. 1.6). If such a volume can be found, then the porosity becomes only a function of the time t and the position $\boldsymbol{x}$ in which the region $\mathcal{R}$ is located, i.e., we derive the fields $n(\boldsymbol{x}, t)$ and $\nu(\boldsymbol{x}, t)$. In particular, if the porous material is dry and its solid matrix has a constant mass density γ, then the mass density field of the medium $\varrho(\boldsymbol{x}, t)$ can be related to n and ν through

$$\varrho = \gamma\nu = \gamma\,(1 - n) \ , \tag{1.6}$$

and the material parameter γ is named *true mass density*. This motivates also a more general definition of ϱ, valid even when the solid matrix is compressible, viz.

$$\varrho(\mathcal{R},t)=\frac{1}{V_{\mathcal{R}}}\int\limits_{\mathcal{R}}\gamma_{\mathtt{D}}\nu_{\mathtt{D}}\,\mathrm{d}^3r\ , \tag{1.7}$$

where $\gamma_{\mathtt{D}}(\boldsymbol{r},t)$ represents the true mass density distribution, i.e., the instantaneous value of the mass density at every microscale position $\boldsymbol{r}$.

Finally, it must be noticed that (1.1)–(1.5) are suited for dry porous media made of a single constituent solid matrix. The appropriate generalizations for saturated and unsaturated multicomponent porous media are nonetheless straightforward on account of the implicit additivity assumed for n, ν, $n_{\mathtt{D}}$ and $\nu_{\mathtt{D}}$. Effectively, let the porous medium be a multicomponent mixture of $N=N_{\mathrm{s}}+N_{\mathrm{f}}$ *immiscible* media[5], so that the first N_{s} constituents form the solid matrix, whose void space is partially/totally filled with the next N_{f} fluid constituents. Basing on this scheme, the volume fraction of every constituent can be written as ν^α ($\alpha=1,2,\ldots,N$), implying that

$$\nu=\sum_{\alpha=1}^{N_{\mathrm{s}}}\nu^\alpha\ ,\qquad\qquad n=\nu^0+\sum_{\alpha=N_{\mathrm{s}}+1}^{N}\nu^\alpha\ , \tag{1.8}$$

where ν^0 stands for the volume fraction of an eventually remaining empty space within the pore volume. Hence, the saturation condition can now be expressed as $\nu^0=0$, while for a dry porous medium $n=\nu^0$ holds. Further, there follow the definitions

$$\nu^\alpha\,(\mathcal{R},t)=\frac{1}{V_{\mathcal{R}}}\int\limits_{\mathcal{R}}\nu_{\mathtt{D}}^\alpha\,\mathrm{d}^3r\ , \tag{1.9}$$

$$\nu_{\mathtt{D}}^\alpha(\boldsymbol{r},t)=\begin{cases}1 & \text{for } \boldsymbol{r} \text{ within the } \alpha\text{-th constituent,}\\ 0 & \text{otherwise,}\end{cases} \tag{1.10}$$

where $\nu_{\mathtt{D}}^\alpha$ denotes the *distribution of the constituent* α. Of course, the volume fraction of the empty space can be defined in a similar manner, by simply setting $\alpha=0$ in (1.9) and (1.10).

1.4 Additional Remarks on the Homogenization of Porous Media

Before closing this chapter, there are some conspicuous features of the process of averaging which are worth noticing. Firstly, according to the arguments presented in Sect. 1.3, a successful homogenization procedure relies on the possibility of finding a suitable volume $V_{\mathcal{R}}$, called REV, which minimizes undesirable oscillations without impairing the construction of a field theory. Nevertheless, it should be emphasized that things are not so simple: continuum theories normally involve the consideration of more than a unique field property (i.e., they usually concern a certain number of fields, like density, pressure, energy, etc.) and consequently, the homogenization of any heterogeneous medium can only be accomplished if there exists, at any time, a

[5]The case of miscible media is more delicate and will be left to Chap. 3.

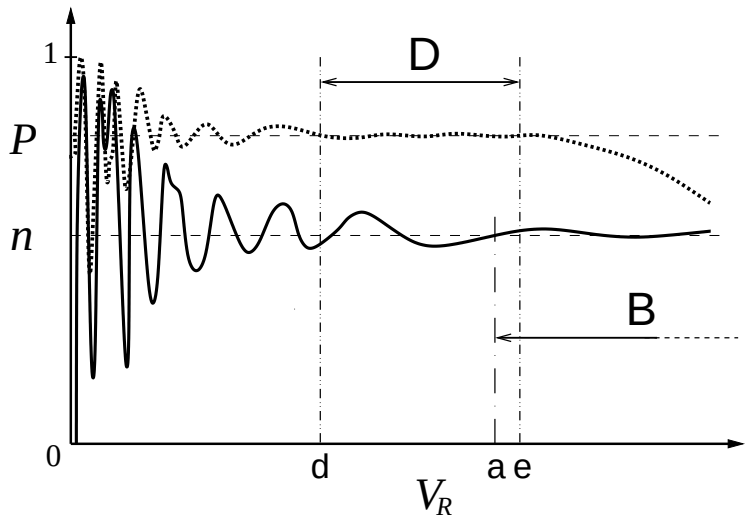


Fig. 1.7. Simultaneous variations of porosity $n(\mathcal{R}, t)$ (solid line) and normalized pressure $P(\mathcal{R}, t)$ (dotted line) as functions of the representative volume $V_{\mathcal{R}}$. Sectors D and B define the range of values of $V_{\mathcal{R}}$ for which homogenization is possible *either* for pressure *or* for porosity, respectively. The points d and e denote the extrema of sector D, while the point a indicates the minimum of sector B. The maximum of sector B lies outside the plot and therefore is not shown. In this example, only values of $V_{\mathcal{R}}$ lying within the overlapping of sectors B and D (i.e., the short volume interval enclosed by the extrema a and e) can be used for the homogenization of the medium

common representative volume $V_{\mathcal{R}}$ for *all* quantities involved in the thermomechanical description of the material.

A simple illustration of this assertion is sketched in Fig. 1.7, for the case of a porous medium saturated with gas. The variations of porosity $n(\mathcal{R}, t)$ and of a normalized pressure $P(\mathcal{R}, t)$, defined by

$$P = \frac{p}{p_0} \ , \qquad p = p(\mathcal{R}, t) \ , \qquad p_0 = \max(p) \ , \tag{1.11}$$

are plotted as functions of the volume of the region $\mathcal{R}$. It can be concluded from that figure that only a very short range of volumes, lying between the extrema a and e, is available for the homogenization of this particular porous material. If any other value of $V_{\mathcal{R}}$ outside this range is employed, false results do emerge.

A second illustrative example is given by the wave propagation problem: it is impossible to describe, within the frames of a homogenized continuum theory, the propagation of an acoustic wave through an interstitial fluid when its wave length is smaller than (or of the order of) the pore size. Any attempt to homogenize the porous medium would smear out the whole wave.

Finally, another instance in which no satisfactory representative volume can easily be found occurs when the medium has double porosity [338], e.g. when the solid matrix itself is porous on a finer scale [47]. In this situation, the strong oscillations of porosity illustrated in the sector A of Fig. 1.6 first evanesce, but then reappear as the volume $V_{\mathcal{R}}$ of the region $\mathcal{R}$ increases. Clearly, the elementary approach discussed above cannot be applied for such media without modifications.

Fortunately, in spite of the strength of these restrictions, situations in which homogenization cannot be attained compose the exception, and not the rule.

2. Stresses and Couple Stresses in Granular Media

The physics of granular materials comes from an illustrious lineage. It includes names like Coulomb during the reign of Louis XVI, Faraday and Reynolds in the nineteenth century, and Bagnold, a remarkable Englishman who became enthralled by the sands of the desert, perhaps even more so than T.E. Lawrence, to the point that he resolved to understand its laws.

Pierre-Gilles de Gennes, in [111] p. v

When talking about porous media, as e.g. in Sects. 1.3 and 1.4, the basic concern is the porous structure and the percolation of interstitial fluids through the voids of the solid matrix, which behaves to some extent like an elastic or nearly rigid skeleton (as e.g. in aquifers, earth dams and geological oil reservoirs [30, 142, 175, 176, 192, 309, 368]). It should be observed, however, that in many situations such a skeleton is in fact made of an aggregate of grains, which – under appropriate circumstances – may fluidify, i.e., it may flow like a fluid (typical examples are debris flows, landslides and snow avalanches [222, 226, 227, 371, 396, 398]). In such situations, the interactions of the solid grains with the surrounding fluid and other grains become crucial, and thence one speaks about *granular media*. On the other hand, a static solid matrix may also be regarded as granular material when the focus is on the network of contact forces or the stability of static arches [111, 284, 357, 359], instead of percolation phenomena. In these cases, the aggregate may even support moderate loads without collapse, in a sort of solid-like behavior. The fascination for granular media owes exactly to this kind of "multiple personality": sometimes solid, other times liquid or even gaseous. Such a polyvalent behavior will be illustrated in this Chapter, which deals with a very simple type of granular medium in order to introduce gradually, in an intuitive manner, the important concepts of stress and couple stress in microstructured continua. Additionally, a complementary discussion on homogenization prepares the reader with a solid background for the latter comprehension of the tenets of continuous diversity.

2.1 Monodisperse aggregates of spheres

As a rule of thumb, whenever one attempts to homogenize a granular medium, two fundamental questions immediately arise:

➢ How should the grains be characterized? (In other words, what are the relevant properties of the granules?)
➢ And how should these grains interact?

Unfortunately, general answers to these questions do not exist. In fact, depending on the situation, different grain characteristics (implying therefore different types of interactions) may play the most crucial role in the material response.

For instance, recalling the example discussed in Sect. 1.1, it does not really matter if the "grains" (i.e., brushstrokes) are all of the same size and shape or not; provided that no huge differences exist, the homogenized result will be essentially the same. Similarly, by considering the statics of a sandpile, slight variations in grain constitution are of minor significance, whereas when the same sandpile is creeping, implying that particle segregation and abrasional effects become important, even small differences in the mass density or roughness of the grains might produce pregnant issues. Finally, if the former sandpile experiences a strong flow with pronounced reduction in the solid phase concentration (e.g., when the grains are blown away by turbidity currents in air or water), then it happens that small variations in grain properties turn to be irrelevant again (except, of course, in a small critical size range).

In spite of these difficulties, from the mechanical viewpoint just a few grain characteristics usually suffice to distinguish them, namely size, shape, roughness, mass density and resilience. Moreover, in most cases (fortunately) not all these properties must be considered simultaneously, and the choice of the leading characteristics is more or less a straightforward matter of wisdom.

From the discussion above, it turns out that one of the simplest conceivable kinds of granular material is a dry cohesionless[1] aggregate of identical hard[2] spheres. This is a particular member of a class of single phase heterogeneous media called *monodisperse* (media), characterized by equal size, shape and constitution of all grains. Thence, concerning this particular medium, the questions posed at the beginning of this Section can be answered as follows:

➢ The grains are assumed to be identical, hard, rough, massive spheres of radius a, which can only be distinguished by their individual instantaneous position (more exactly, the position of their respective centers of mass).
➢ They interact solely by physical contact, be this lasting (static) or sudden (collisional). The prescription of appropriate explicit expressions for the contact forces, even in the simplest cases, is one of the most challenging tasks of the theory of granular media, since it must include realistic descriptions of intricate frictional and dissipative effects, and is therefore beyond the scope of this work. Nevert-

[1]Cohesion is defined as the ability of a granular aggregate to support tensile loads. It stems from surface attractive (adhesive) forces acting at grain contacts, which might have several physico-chemical causes (e.g. surface tension of the interstitial fluid or electrostatic interactions).

[2]In the jargon of the theory of granular media, the adjective "hard" does not mean that the collisions are elastic – this would be fully unrealistic for granular matter, where dissipation plays a decisive role. It simply means that the grains have negligible deformation during collision (i.e., they remain "rigid") and consequently that intergranular fields of stress, couple stress, etc. are uniform. The dissipation of energy during collision is described in this case by a *coefficient of elastic restitution* (or *restriction*) $0 \leq \varepsilon \leq 1$, such that $\varepsilon = 0$ ($\varepsilon = 1$) for completely inelastic (perfectly elastic) collisions [111, 224].

heless, implicit references to contact forces will be necessary when dealing with stresses and couple stresses.

The homogenization of such a monodisperse aggregate of spheres is attractive due to its relative simplicity: the averaging procedure is nearly straightforward and it gives just rise to an *isotropic single continuum*.

Clearly, from a dynamical perspective, one of the most essential fields of this continuum is the translational velocity $\boldsymbol{v}$. Owing to the similitude of the grains, a first attempt to define $\boldsymbol{v}$ would simply be based on a trivial arithmetic mean

$$\boldsymbol{v}(\mathcal{R},t)=\frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\boldsymbol{v}^{\mathfrak{g}}\ , \tag{2.1}$$

although a more comprehensive definition, valid on any scale, should consider the weighted average

$$\boldsymbol{v}(\mathcal{R},t)=\frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\boldsymbol{v}^{\mathfrak{g}}w^{\mathfrak{g}}\ , \tag{2.2}$$

where $N_{\mathcal{R}}$ represents the number of grains enclosed in the representative region $\mathcal{R}\subset\mathbb{R}^3$, $\boldsymbol{v}^{\mathfrak{g}}$ is the velocity of the $\mathfrak{g}$-th grain and $w^{\mathfrak{g}}$ is a confining weight factor which can assume values equal to or less than unity, depending on whether the $\mathfrak{g}$-th granule is completely or only partially enclosed within the region $\mathcal{R}$. Evidently, (2.1) and (2.2) converge to the same result when $N_{\mathcal{R}}$ is sufficiently large. Within the context of Sect. 1.3, this convergence corresponds to the finding of a suitable representative elementary volume (REV), which minimizes undesirable oscillations and is insensitive to (moderate) variations of size and/or shape of the region $\mathcal{R}$. Once the focus of this work is precisely on such situations, which conform with the continuum hypothesis introduced in Sect. 1.2, it will be tacitly assumed from now on that $N_{\mathcal{R}}$ *may be so large as necessary to ensure the validity of the continuum hypothesis and the definition of a convenient* REV*, in the sense discussed above.* Consequently, (2.1) and (2.2) can be now rewritten as

$$\boldsymbol{v}(\boldsymbol{x},t)=\frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\boldsymbol{v}^{\mathfrak{g}}\ . \tag{2.3}$$

Although (2.3) is indeed the desired expression for the translational velocity in the present case, one could wonder if a more general definition, in the spirit of Sect. 1.3, could be derived. Actually, the answer is yes – once it is recognized that the *linear momenta of the grains*, instead of their velocities, should be considered during the averaging process (since they are additive quantities, while the velocities are not). Effectively, denoting the density of linear momentum of the aggregate by $\varrho\boldsymbol{v}$, where the mass density ϱ is derived via (1.6) or (1.7), the following general definition can be introduced (cf. (1.1), (1.2) and (1.7)):

$$\varrho\boldsymbol{v}(\boldsymbol{x},t)=\frac{1}{V_{\mathcal{R}}}\int\limits_{\mathcal{R}}\gamma_{\mathtt{D}}\boldsymbol{v}_{\mathtt{D}}\,\mathrm{d}^3r\ , \tag{2.4}$$

where $\boldsymbol{v}_{\mathtt{D}}(\boldsymbol{r},t)$ denotes the velocity distribution in $\mathcal{R}$, while $\gamma_{\mathtt{D}}$ stands for the true mass density distribution already introduced in (1.7). It is important to notice that, for a dry granular medium[3], the distribution $\boldsymbol{v}_{\mathtt{D}}$ vanishes identically in every point of the pore space, implying the *equipollence relation* $\boldsymbol{v}_{\mathtt{D}} = \nu_{\mathtt{D}}\boldsymbol{v}_{\mathtt{D}}$ (cf. (1.4)). On the other hand, for the particular monodisperse aggregate of spheres considered here, there holds $\gamma_{\mathtt{D}} = \gamma\nu_{\mathtt{D}}$ ($\gamma = \text{const.}$) and the integral of $\boldsymbol{v}_{\mathtt{D}}$ over the volume of the $\mathfrak{g}$-th grain yields $\nu V_{\mathcal{R}}\boldsymbol{v}^{\mathfrak{g}}/N_{\mathcal{R}}$. Consequently, (2.3) is recovered.

In addition to translational motion, it is evident that granules may also rotate. As a rule, the rotational motion of any particle (with respect to its center of mass), be it a grain, a molecule or a material point, is described by an intrinsic angular momentum called *spin* [78, 84, 88]. Associated to it, there is the *spin velocity*, generically defined for any kind of granular medium through the relations

$$\boldsymbol{\sigma} = \mathbf{I}\,\boldsymbol{s}\ , \qquad\qquad \boldsymbol{\sigma}^{\mathfrak{g}} = \mathbf{I}^{\mathfrak{g}}\boldsymbol{s}^{\mathfrak{g}}\ , \tag{2.5}$$

where $\boldsymbol{\sigma}$, $\mathbf{I}$, $\boldsymbol{s}$ and $\boldsymbol{\sigma}^{\mathfrak{g}}$, $\mathbf{I}^{\mathfrak{g}}$, $\boldsymbol{s}^{\mathfrak{g}}$ represent the specific spins, inertia tensors and spin velocities of the aggregate and of the $\mathfrak{g}$-th grain, respectively. In particular, for the special type of granular medium presently considered, the spin velocity can be calculated in a similar manner as the translational velocity $\boldsymbol{v}$ (see (2.1)–(2.4)), viz. by exploiting the additivity of its respective momentum, the spin. Effectively, by analogy with (2.1),

$$\boldsymbol{\sigma}(\boldsymbol{x},t) = \frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\boldsymbol{\sigma}^{\mathfrak{g}}\ . \tag{2.6}$$

Since spin inertia is also an additive property, one would expect a relation of the similar form, viz.

$$\mathbf{I} = \frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\mathbf{I}^{\mathfrak{g}}\ , \tag{2.7}$$

which is nevertheless redundant, for it is derived under the condition that all grains are spherically identical, which obviously implies

$$\mathbf{I} = \mathbf{I}^{\mathfrak{g}} = R^2\mathbf{1}\ , \tag{2.8}$$

with $R = a\sqrt{2/5}$ denoting the radius of gyration of a massive sphere of radius a, while $\mathbf{1}$ is the unit tensor (whose Cartesian components are $\mathbf{1}_{ij} = \delta_{ij}$, where δ_{ij} is the Kronecker delta). Consequently, in the present case (2.5)–(2.7) yields

$$\boldsymbol{s} = \frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\boldsymbol{s}^{\mathfrak{g}}\ . \tag{2.9}$$

This is a very special result, valid only for aggregates of identical spheres.

In direct analogy to the general definitions (1.1), (1.3), (1.7) and (2.4), generic counterparts of the particular relations (2.6) and (2.7) can be proposed, viz.

[3] An extension of these results for the case of (un-)saturated media is straightforward, in view of (1.8)–(1.10).

$$\varrho\boldsymbol{\sigma}(\boldsymbol{x},t)=\frac{1}{V_{\mathcal{R}}}\int\limits_{\mathcal{R}}\gamma_{\mathtt{D}}\boldsymbol{\sigma}_{\mathtt{D}}\,\mathrm{d}^3r\;,\qquad\qquad\varrho\mathbf{I}(\boldsymbol{x},t)=\frac{1}{V_{\mathcal{R}}}\int\limits_{\mathcal{R}}\gamma_{\mathtt{D}}\mathbf{I}_{\mathtt{D}}\,\mathrm{d}^3r\;,\tag{2.10}$$

while the spin velocity $\boldsymbol{s}$ is still derived via $(2.5)_1$. As usual, the quantities $\boldsymbol{\sigma}_{\mathtt{D}}$ and $\mathbf{I}_{\mathtt{D}}$ stand for the distributions of spin and its inertia within the region $\mathcal{R}$. They are null everywhere outside the grains, implying thence the equipollence relations $\boldsymbol{\sigma}_{\mathtt{D}}=\nu_{\mathtt{D}}\boldsymbol{\sigma}_{\mathtt{D}}$ and $\mathbf{I}_{\mathtt{D}}=\nu_{\mathtt{D}}\mathbf{I}_{\mathtt{D}}$.

In order to prove that (2.6) and (2.7) are indeed derivable from (2.10), one must first recognize that the vanishing of $\boldsymbol{\sigma}_{\mathtt{D}}$ and $\mathbf{I}_{\mathtt{D}}$ outside the grains allows one to split both $(2.10)_1$ and $(2.10)_2$ into sums of integrals over the volumes of the individual granules. More specifically, consider for instance the case of the spin inertia (analogous arguments hold also for the spin): its distribution is explicitly given by

$$\mathbf{I}_{\mathtt{D}}(\boldsymbol{r},t)=\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\mathbf{I}_{\mathtt{D}}^{\mathfrak{g}}\;,\tag{2.11}$$

with

$$\mathbf{I}_{\mathtt{D}}^{\mathfrak{g}}(\boldsymbol{r},t)=\begin{cases}[(l^{\mathfrak{g}})^2\mathbf{1}-\boldsymbol{l}^{\mathfrak{g}}\otimes\boldsymbol{l}^{\mathfrak{g}}] & \text{for } \boldsymbol{r} \text{ within the } \mathfrak{g}\text{-th grain,}\\ 0 & \text{otherwise.}\end{cases}\tag{2.12}$$

The vector $\boldsymbol{l}^{\mathfrak{g}}$ represents the distance of the position $\boldsymbol{r}$ from the center of mass of the $\mathfrak{g}$-th grain $\boldsymbol{r}^{\mathfrak{g}}$, viz.

$$\boldsymbol{l}^{\mathfrak{g}}=\boldsymbol{r}-\boldsymbol{r}^{\mathfrak{g}}\;,\qquad\text{and}\qquad(l^{\mathfrak{g}})^2=\boldsymbol{l}^{\mathfrak{g}}\cdot\boldsymbol{l}^{\mathfrak{g}}\;.\tag{2.13}$$

Insertion of (2.11)–(2.13) into $(2.10)_2$ leads to (2.7) and the identity

$$\mathbf{I}^{\mathfrak{g}}=\frac{1}{V^{\mathfrak{g}}}\int\limits_{\mathcal{R}}\mathbf{I}_{\mathtt{D}}^{\mathfrak{g}}\,\mathrm{d}^3r\qquad\qquad\left(\text{with}\quad V^{\mathfrak{g}}=\frac{\nu V_{\mathcal{R}}}{N_{\mathcal{R}}}=\frac{4\pi a^3}{3}\right).\tag{2.14}$$

Notice that the only part of $\mathcal{R}$ in which the above integral does not vanish is the one occupied by the $\mathfrak{g}$-th grain. Finally, the integral in (2.14) can be easily computed after a simple change of variables $\boldsymbol{r}\to\boldsymbol{l}^{\mathfrak{g}}$. It yields the result $\mathbf{I}^{\mathfrak{g}}=(2a^2/5)\mathbf{1}=R^2\mathbf{1}$, just as expected.

Once the kinetics of granular media is understood, the next step concerns the study of the driving forces of motion, viz. stresses and couple stresses.

2.2 Collisions, time averaging and stress

As attention is turned towards stress, one arrives at the essence of the mechanics of granular media: contact forces and collisions. Except for utterly static situations, these processes introduce unavoidable temporal singularities, which must of course be smoothened in a final continuum description. It is not the intention of this work, however, to dwell upon time averaging procedures, provided that the scope of this

chapter is on spatial heterogeneities, and not on temporal discontinuities. Just a few comments will be eventually given when necessary, and the reader interested in more details is referred to the specialized literature on the subject [5, 32, 111, 117, 206, 258, 282, 285, 313].

In particular, a general remark is that all averages considered so far, as well as those going to be presented in the sequel, are in fact of instantaneous nature, i.e., they are performed for a fixed time instant t. In this sense, they can be regarded as instantaneously homogenized "snapshots" of the ongoing processes. In applications (see e.g. [64–66, 258, 259]), temporal discontinuities are smeared out by averaging over many of these snapshots, in a manner somewhat similar to an ensemble average [30, 66]. In the simplest situations, this corresponds to integrate the instantaneously homogenized quantities (say, (2.4)) over some representative time interval[4], with further normalization of the result by the averaging period. More specifically, for the particular case of the monodisperse aggregate of spheres considered in the last section, this time averaging reduces simply to an arithmetic mean of a given number of sequential snapshots. At last, the choice of the averaging period depends on the characteristics of the process, specially on the collision rate.

The occurrence of collisions makes evident that each grain of any cohesionless granular medium must everywhen be in one of two possible circumstances: either in contact interaction with walls and other grains, or in "free flight" (no contacts at all). These situations characterize the two fundamental modes of momentum flux, namely via mass transport and contact transfer. In continuum mechanics, the first one comprises the so-called *convective and diffusive fluxes*, while the last one is often associated to *conductive fluxes* [132, 209]. In particular, for the case of linear momentum, its corresponding non-convective influx is known as *stress*.

From the above arguments, one concludes that the stress in a granular medium should consist of at least two parts, one due to contact forces (called *contact stress*) and another one due to "free flight" diffusive motion (named *diffusive* or *streaming stress*). Explicit expressions for these two contributions have been suggested in the literature as follows.

Streaming stress: Some authors (e.g. [64–66]) have suggested an interpretation of the (auto-)diffusive velocity of the $\mathfrak{g}$-th grain, viz.

$$\boldsymbol{C}^{\mathfrak{g}} = \boldsymbol{v}^{\mathfrak{g}} - \boldsymbol{v} \ , \tag{2.15}$$

as a kind of "fluctuation" of the grain velocity $\boldsymbol{v}^{\mathfrak{g}}$ with respect to the macroscale motion $\boldsymbol{v}$, so as to propose a gross analogy of the streaming stress in granular materials with the Reynolds stress of turbulence theory [300], which is given by

$$-\varrho \left\langle \tilde{\boldsymbol{C}} \otimes \tilde{\boldsymbol{C}} \right\rangle \ , \tag{2.16}$$

[4]Clearly, the representative time interval (or even better, *representative elementary time* (RET) [30]) is a temporal counterpart of the representative elementary volume (REV) introduced in Sect. 1.3. Consequently, it might be regarded as a "macroscale time instant", being thence subjected to restrictions equivalent to those discussed in Sects. 1.3 and 1.4.

where $\tilde{\boldsymbol{C}}$ is a (real) velocity fluctuation, while the angular brackets $\langle\cdot\rangle$ denote time average. Furthermore, kinetic theories of granular flow [234, 286] have also given support to expressions somewhat analogous to (2.16), in which this term is named *kinetic part of stress* and the angular brackets have the meaning of an ensemble average in the space of velocities. Consequently, for the particular case of the monodisperse aggregate of spheres considered in Sect. 2.1, one would conjecture a streaming stress of the form[5]

$$-\varrho\left(\frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\boldsymbol{C}^{\mathfrak{g}}\otimes\boldsymbol{C}^{\mathfrak{g}}\right)\,, \tag{2.17}$$

where the term within round brackets represents an arithmetic averaging over $N_{\mathcal{R}}$ grains (cf. (2.1)).

Contact stress: On the authority of Love [281], the definition of contact stress in an aggregate can be traced back to the work of Cauchy, in the first half of the 19th century. Since then, it has become well established in the literature that the contact stress in a region $\mathcal{R}$ of the granular medium is equal to the average of the contact stresses in the enclosed grains [76, 105, 233, 258, 259]. Accordingly, the contact stress in the particular monodisperse aggregate of spheres under study is expected to be given by the arithmetic mean

$$\frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\mathbf{t}^{\mathfrak{g}}\,,\qquad\text{with}\qquad\mathbf{t}^{\mathfrak{g}}=\frac{a}{V^{\mathfrak{g}}}\sum_{\mathfrak{k}=1}^{K^{\mathfrak{g}}}\boldsymbol{F}^{\mathfrak{g}\mathfrak{k}}\otimes\boldsymbol{k}^{\mathfrak{g}\mathfrak{k}}\,, \tag{2.18}$$

where $\mathbf{t}^{\mathfrak{g}}$ and $K^{\mathfrak{g}}$ are respectively the granular stress and the number of contacts in the $\mathfrak{g}$-th grain (of radius a), $\boldsymbol{k}^{\mathfrak{g}\mathfrak{k}}$ is the unit branch vector pointing from the center of mass of the $\mathfrak{g}$-th grain to its $\mathfrak{k}$-th contact point, $\boldsymbol{F}^{\mathfrak{g}\mathfrak{k}}$ is the force acting on the $\mathfrak{k}$-th contact of grain $\mathfrak{g}$, and $V^{\mathfrak{g}}$ is the grain volume, defined in (2.14). Equation $(2.18)_2$ – or a symmetrized version of it – has been derived via heuristic and/or statistical arguments (sometimes combined with the principle of virtual work) [27, 76, 105, 302, 358] and can be interpreted as follows: $\boldsymbol{F}^{\mathfrak{g}\mathfrak{k}}/V^{\mathfrak{g}}$ represents a density of impulse rate, i.e. the amount of linear momentum (per unit volume) transferred per unit time along a distance a from the $\mathfrak{k}$-th contact to the center of mass of the $\mathfrak{g}$-th grain.

Consequently, the combination of (2.17) and (2.18) yields the homogenized stress for the example of an aggregate of identical spheres[6]

$$\mathbf{t}(\boldsymbol{x},t)\;=\;\frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\left(\frac{a}{V^{\mathfrak{g}}}\sum_{\mathfrak{k}=1}^{K^{\mathfrak{g}}}\boldsymbol{F}^{\mathfrak{g}\mathfrak{k}}\otimes\boldsymbol{k}^{\mathfrak{g}\mathfrak{k}}\right)\;-\;\varrho\left(\frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\boldsymbol{C}^{\mathfrak{g}}\otimes\boldsymbol{C}^{\mathfrak{g}}\right)\,. \tag{2.19}$$

[5] In view of the remarks presented at the beginning of this section, time averaging is omitted for brevity.

[6] Instead of the double sum in the first term of (2.19), some authors have used a single sum over all contact points within the region $\mathcal{R}$ or on its boundary. The equivalence between all these expressions has been demonstrated by Lätzel et al. [258].

Now, the experience acquired through the generic definitions (1.1), (1.3), (1.7), (2.4) and (2.10) provides motivation to propose a generalization also of the results (2.17)–(2.19). In order to achieve this, however, it will be necessary to invoke in advance some important concepts which are going to be presented in detail only later on. In particular, recalling that $\mathbf{t}$ is a non-convective flux, it follows that this quantity should be compatible with the *generic definition of non-convective flux* (3.15) – which will be exhaustively discussed in Sect. 3.2 – allowing one to put forward the following *general definition of homogenized stress*:

$$\mathbf{t}(\boldsymbol{x},t) \;=\; \frac{1}{V_{\mathcal{R}}}\int\limits_{\mathcal{R}} \left(\mathbf{t}_{\mathtt{D}} - \gamma_{\mathtt{D}}\boldsymbol{v}_{\mathtt{D}}\otimes\boldsymbol{C}_{\mathtt{D}}\right)\,\mathrm{d}^3r\;, \tag{2.20}$$

where $\gamma_{\mathtt{D}}$ and $\boldsymbol{v}_{\mathtt{D}}$ are the distributions of true mass density and translational velocity, respectively, already defined in (1.7) and (2.4). Further, $\mathtt{t}_{\mathtt{D}}$ is the *conductive stress distribution* within the region $\mathcal{R}$, while

$$\boldsymbol{C}_{\mathtt{D}}(\boldsymbol{r},t) = \nu_{\mathtt{D}}\left(\boldsymbol{v}_{\mathtt{D}} - \boldsymbol{v}\right) \tag{2.21}$$

denotes the *relative* (also *diffusive*) *velocity distribution*.

Hence, (2.20) states that linear momentum can be transmitted not only by conduction (via $\mathbf{t}_{\mathtt{D}}$), but also by diffusion, in which an amount $\gamma_{\mathtt{D}}\boldsymbol{v}_{\mathtt{D}}$ of linear momentum is transported through the medium at relative velocity $\boldsymbol{C}_{\mathtt{D}}$. Finally, because of (1.7), (2.4) and (2.21), it is straightforward to verify the helpful identities

$$\int\limits_{\mathcal{R}} \gamma_{\mathtt{D}}\boldsymbol{C}_{\mathtt{D}}\,\mathrm{d}^3r = \mathbf{0}\;, \qquad \text{and} \qquad \int\limits_{\mathcal{R}} \gamma_{\mathtt{D}}\boldsymbol{v}_{\mathtt{D}}\otimes\boldsymbol{C}_{\mathtt{D}}\,\mathrm{d}^3r \;=\int\limits_{\mathcal{R}} \gamma_{\mathtt{D}}\boldsymbol{C}_{\mathtt{D}}\otimes\boldsymbol{C}_{\mathtt{D}}\,\mathrm{d}^3r\;, \tag{2.22}$$

which can be used to eliminate $\boldsymbol{v}_{\mathtt{D}}$ from (2.20), establishing so the symmetry of the streaming stress.

There remains to prove that (2.19) can indeed be derived as a particular case of (2.20). Effectively, for a dry granular medium one can without loss of generality decompose the integrand of (2.20) into individual granular contributions (cf. (2.11)–(2.13))

$$\mathbf{t}_{\mathtt{D}} - \gamma_{\mathtt{D}}\boldsymbol{C}_{\mathtt{D}}\otimes\boldsymbol{C}_{\mathtt{D}} = \sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\left(\mathbf{t}_{\mathtt{D}}^{\mathfrak{g}} - \gamma_{\mathtt{D}}^{\mathfrak{g}}\boldsymbol{C}_{\mathtt{D}}^{\mathfrak{g}}\otimes\boldsymbol{C}_{\mathtt{D}}^{\mathfrak{g}}\right)\;, \tag{2.23}$$

in such a way that the granular distributions $\mathbf{t}_{\mathtt{D}}^{\mathfrak{g}}$, $\gamma_{\mathtt{D}}^{\mathfrak{g}}$ and $\boldsymbol{C}_{\mathtt{D}}^{\mathfrak{g}} = \nu_{\mathtt{D}}^{\mathfrak{g}}\left(\boldsymbol{v}_{\mathtt{D}}^{\mathfrak{g}} - \boldsymbol{v}\right)$ all vanish everywhere outside the $\mathfrak{g}$-th grain. Insertion of (2.23) into (2.20) leads then to

$$\mathbf{t}(\boldsymbol{x},t) \;=\; \frac{1}{V_{\mathcal{R}}}\int\limits_{\mathcal{R}} \sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\left(\mathbf{t}_{\mathtt{D}}^{\mathfrak{g}} - \gamma_{\mathtt{D}}^{\mathfrak{g}}\boldsymbol{C}_{\mathtt{D}}^{\mathfrak{g}}\otimes\boldsymbol{C}_{\mathtt{D}}^{\mathfrak{g}}\right)\,\mathrm{d}^3r\;, \tag{2.24}$$

which after interchange of the order of summation and integration yields (with the aid of (1.6), (1.7) and $\varrho^{\mathfrak{g}} = \gamma^{\mathfrak{g}} = \gamma$)

$$\mathbf{t}(\boldsymbol{x},t) \;=\; \frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\mathbf{t}^{\mathfrak{g}} \;-\; \varrho\left(\frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\boldsymbol{C}^{\mathfrak{g}}\otimes\boldsymbol{C}^{\mathfrak{g}}\right)\;. \tag{2.25}$$

The granular stress $\mathbf{t}^{\mathfrak{g}}$ is now given by

$$\mathbf{t}^{\mathfrak{g}} = \frac{1}{V^{\mathfrak{g}}}\int\limits_{\mathcal{R}}\left(\mathbf{t}_{\mathtt{D}}^{\mathfrak{g}} - \gamma_{\mathtt{D}}^{\mathfrak{g}}\boldsymbol{C}_{\mathtt{D}}^{\mathfrak{g}}\otimes\boldsymbol{C}_{\mathtt{D}}^{\mathfrak{g}}\right)\,\mathrm{d}^3r\;, \tag{2.26}$$

with $V^{\mathfrak{g}}$ defined as in (2.14) and $\boldsymbol{C}_{\mathtt{D}}^{\mathfrak{g}}$ denoting the relative velocity of an interior point of the $\mathfrak{g}$-th grain with respect to the velocity of its center of mass, i.e.,

$$\boldsymbol{C}_{\mathtt{D}}^{\mathfrak{g}} = \nu_{\mathtt{D}}^{\mathfrak{g}}\left(\boldsymbol{v}_{\mathtt{D}}^{\mathfrak{g}} - \boldsymbol{v}^{\mathfrak{g}}\right) = \nu_{\mathtt{D}}^{\mathfrak{g}}\left(\boldsymbol{C}_{\mathtt{D}}^{\mathfrak{g}} - \boldsymbol{C}^{\mathfrak{g}}\right)\;. \tag{2.27}$$

At this moment, it is important to behold the refined meaning of the second integral on the right-hand side of (2.26): it describes diffusive effects occurring *inside* the grain, usually arising from deformation. Consequently, this term should vanish for the case of rigid spheres considered here[7]. Besides that, it should be emphasized that only the part $\mathcal{G}^{\mathfrak{g}} \subset \mathcal{R}$ which is momentarily occupied by the $\mathfrak{g}$-grain plays a role in the integral (2.26). Ergo, provided that (by definition) the $\mathfrak{g}$-th granule can only be specified when the instantaneous position of its center of mass $\boldsymbol{r}^{\mathfrak{g}}$ is known, the $\boldsymbol{r}$-dependence of $\mathbf{t}_{\mathtt{D}}^{\mathfrak{g}}$ can be re-expressed in terms of the relative position $\boldsymbol{l}^{\mathfrak{g}}$ introduced in (2.13), in such a way that, by performing a simple change of variables $\boldsymbol{r} \rightarrow \boldsymbol{l}^{\mathfrak{g}}$, (2.26) reduces to

$$\mathbf{t}^{\mathfrak{g}} = \frac{1}{V^{\mathfrak{g}}}\int\limits_{\mathcal{G}^{\mathfrak{g}}}\mathbf{t}_{\mathtt{D}}^{\mathfrak{g}}\,\mathrm{d}^3l\;, \tag{2.28}$$

which is nothing else than an average of the intragranular stress distribution $\mathbf{t}_{\mathtt{D}}^{\mathfrak{g}}$, performed only over the volume of the $\mathfrak{g}$-th grain, and with respect to a local reference frame centered on $\boldsymbol{r}^{\mathfrak{g}}$, in such a manner that positions are now described by $\boldsymbol{l}^{\mathfrak{g}}$ (d^3l represents its respective volume element).

Keeping these concepts in mind – in particular the fact that $\boldsymbol{l}^{\mathfrak{g}}$ is temporarily playing the role of position vector, so that $\mathrm{grad} = \partial/\partial\boldsymbol{l}^{\mathfrak{g}}$ – it is possible to solve the integral (2.28) with the aid of the identity

$$\mathrm{grad}\,\boldsymbol{l}^{\mathfrak{g}} = \frac{\partial\boldsymbol{l}^{\mathfrak{g}}}{\partial\boldsymbol{l}^{\mathfrak{g}}} = \mathbf{1}\,, \tag{2.29}$$

which implies

$$\left(\mathbf{t}_{\mathtt{D}}^{\mathfrak{g}}\right)^{\mathsf{T}} = \left(\mathrm{grad}\,\boldsymbol{l}^{\mathfrak{g}}\right)\left(\mathbf{t}_{\mathtt{D}}^{\mathfrak{g}}\right)^{\mathsf{T}} = \mathrm{div}\left(\boldsymbol{l}^{\mathfrak{g}}\otimes\mathbf{t}_{\mathtt{D}}^{\mathfrak{g}}\right) - \boldsymbol{l}^{\mathfrak{g}}\otimes\mathrm{div}\,\mathbf{t}_{\mathtt{D}}^{\mathfrak{g}}\;. \tag{2.30}$$

Insertion of (2.30) into (2.28) leads to

[7] There are many ways of proving that the second integral of (2.26) really vanishes for rigid grains. The most simple is by recognizing that its integrand is independent of the frame of reference (since mass density and relative velocity are invariant quantities). Thence, one can choose a suitable reference frame which moves and rotates with the grain, in such a way that $\boldsymbol{C}_{\mathtt{D}}^{\mathfrak{g}}$ vanishes identically whenever the motion is rigid.

$$(\mathbf{t}^{\mathfrak{g}})^{\mathsf{T}} = \frac{1}{V^{\mathfrak{g}}} \oint\limits_{\partial\mathcal{G}^{\mathfrak{g}}} (\boldsymbol{l}^{\mathfrak{g}} \otimes \mathbf{t}_{\mathrm{D}}^{\mathfrak{g}})\, \boldsymbol{e}\, \mathrm{d}^2 l - \frac{1}{V^{\mathfrak{g}}} \int\limits_{\mathcal{G}^{\mathfrak{g}}} \boldsymbol{l}^{\mathfrak{g}} \otimes \operatorname{div} \mathbf{t}_{\mathrm{D}}^{\mathfrak{g}}\, \mathrm{d}^3 l \;, \tag{2.31}$$

where Gauss' theorem has been applied to transform the first term of (2.31) into a closed surface integral, with $\mathrm{d}^2 l$ denoting a surface element and $\boldsymbol{e}$ its respective normal vector (pointing outwards the surface). For rigid grains, the stress field within the granule may be assumed uniform, implying that $\operatorname{div} \mathbf{t}_{\mathrm{D}}^{\mathfrak{g}} = 0$ in all points within the grain, so that the volume integral on the right-hand side of (2.31) must vanish. Under such circumstances, one obtains

$$\mathbf{t}^{\mathfrak{g}} = \frac{1}{V^{\mathfrak{g}}} \oint\limits_{\partial\mathcal{G}^{\mathfrak{g}}} (\mathbf{t}_{\mathrm{D}}^{\mathfrak{g}} \boldsymbol{e}) \otimes \boldsymbol{l}^{\mathfrak{g}}\, \mathrm{d}^2 l \;. \tag{2.32}$$

The term $\mathbf{t}_{\mathrm{D}}^{\mathfrak{g}} \boldsymbol{e}$ represents a stress vector field, acting on the $K^{\mathfrak{g}}$ contact points $\boldsymbol{l}^{\mathfrak{g}} = a\boldsymbol{k}^{\mathfrak{g}\mathfrak{k}}$ ($\mathfrak{k} = 1, 2, \ldots, K^{\mathfrak{g}}$) lying on the surface $\partial\mathcal{G}^{\mathfrak{g}}$ of the $\mathfrak{g}$-th grain. Assuming for simplicity that such contacts have infinitesimal surface areas $(\delta^2 l)^{\mathfrak{k}}$ over which the applied stress is uniform, one can finally transform (2.32) into the sum

$$\mathbf{t}^{\mathfrak{g}} = \frac{a}{V^{\mathfrak{g}}} \sum_{\mathfrak{k}=1}^{K^{\mathfrak{g}}} \boldsymbol{F}^{\mathfrak{g}\mathfrak{k}} \otimes \boldsymbol{k}^{\mathfrak{g}\mathfrak{k}} \;, \tag{2.33}$$

where $\boldsymbol{F}^{\mathfrak{g}\mathfrak{k}} = (\mathbf{t}_{\mathrm{D}}^{\mathfrak{g}} \boldsymbol{e})(\delta^2 l)^{\mathfrak{k}}$ is the force acting on the $\mathfrak{k}$-th contact of the $\mathfrak{g}$-th grain. Thus, by combining (2.33) with (2.25), the particular relation (2.19) is recovered.

2.3 Torque & couple stress

After a short inspection of (2.25) and (2.33), it can be observed that the stress tensor in a granular medium may generally not be symmetric, due to the presence of the granular stress (2.33). In earlier works [27, 76, 105, 302, 358], some authors have imposed additional assumptions on their models in order to ensure the symmetry of the stress tensor, like e.g. that the forces and couples acting on every grain should always be separately equilibrated, restricting so the validity (2.25) to static situations (and "quasi-static" approximations) in which (2.33) can be symmetrized[8].

In contrast, the derivation presented in Sect. 2.2 does not invoke any restrictive symmetry condition or equilibrium assumption, therefore allowing (2.25) to hold in all regimes, from static to instationary dynamic processes. Actually, on account of the fact that all averages in Sect. 2.2 represent instantaneous "snapshots" of the medium, the distinction between a static contact and a sudden collision is just a matter of duration of the force $\boldsymbol{F}^{\mathfrak{g}\mathfrak{k}}$ (which might be sometimes advantageously interpreted as an impulse rate) and the chosen temporal averaging strategy.

[8] A simpler manner of securing the symmetry of (2.25) would be by assuming that the surface of the spheres is absolutely smooth, so that only normal forces could act on the grains, i.e., $\boldsymbol{F}^{\mathfrak{g}\mathfrak{k}} \times \boldsymbol{k}^{\mathfrak{g}\mathfrak{k}} = 0$. This hypothesis however is physically unreasonable, because it would imply the vanishing of the internal angle of friction – a fundamental property of granular materials, which is responsible e.g. for the stability of arches and sandpiles.

The skew-symmetric part of the stress tensor gives rise to a torque, denoted by the axial vector of stress $\boldsymbol{\vartheta}$, whose Cartesian components read

$$\vartheta_i = \tfrac{1}{2}\epsilon_{ijk}\mathtt{t}_{kj} \ , \tag{2.34}$$

where ϵ_{ijk} denotes the (Levi-Civita) permutation symbol. Accordingly, for the particular example of the already mentioned aggregate of spheres, it follows from (2.25) and (2.33) that

$$\boldsymbol{\vartheta} = -\frac{1}{2}\left[\frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\left(\frac{a}{V^{\mathfrak{g}}}\sum_{\mathfrak{k}=1}^{K^{\mathfrak{g}}}\boldsymbol{F}^{\mathfrak{g}\mathfrak{k}}\times\boldsymbol{k}^{\mathfrak{g}\mathfrak{k}}\right)\right] \ . \tag{2.35}$$

Equation (2.35) clearly indicates that the torque $\boldsymbol{\vartheta}$ acts as a volume source (in fact most commonly a volume sink) of spin. But then comes the question to mind: if a material possesses and produces spin, should it not be capable of transmitting spin as well? One is inevitably tempted to conjecture also about some mechanism of conduction, which could spread spin out; a kind of rotational counterpart to Cauchy stress. Hence, following the motto "*when we start to generalize, it is hard to know when to stop*" (Truesdell [406], p. 24), one can introduce the concept of a non-convective flux of spin, which has been named couple stress, or more specifically, *Voigt couple stress*[9]. Continua which possess spin, torque and couple stress are generally called *Cosserat media* [79, 409].

The interest for torques and couple stresses in granular materials is something relatively recent, and is mainly motivated (but not solely) by the modeling of shear bands as Cosserat continua [64, 65, 98, 117, 233, 259, 314, 329]. In general, the arguments leading to explicit forms of the average couple stress in an aggregate are essentially the same as for the case of stress (see Sect. 2.2). Nevertheless, owing to the special interest on localization phenomena (shear bands), almost all authors have restricted their attention only to the contact contribution to couple stress, which (by analogy with (2.18)) has the form

$$\frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\mathbf{m}^{\mathfrak{g}} \ , \qquad \text{with} \qquad \mathbf{m}^{\mathfrak{g}} = \frac{a^2}{V^{\mathfrak{g}}}\sum_{\mathfrak{k}=1}^{K^{\mathfrak{g}}}\left(\boldsymbol{F}^{\mathfrak{g}\mathfrak{k}}\times\boldsymbol{k}^{\mathfrak{g}\mathfrak{k}}\right)\otimes\boldsymbol{k}^{\mathfrak{g}\mathfrak{k}} \ , \tag{2.36}$$

where $\mathbf{m}^{\mathfrak{g}}$ stands for the granular couple stress, while the meaning of the remaining quantities is the same as in Sects. 2.1 and 2.2 Notwithstanding, Campbell [64, 65] has suggested also an expression for the streaming part of couple stress which is conceptually similar to the streaming stress (2.17), which implies the following arithmetic average for the particular aggregate of spheres under consideration:

$$-\varrho R^2\left(\frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\boldsymbol{S}^{\mathfrak{g}}\otimes\boldsymbol{C}^{\mathfrak{g}}\right) \ . \tag{2.37}$$

[9]The association of Voigt's name to the concept of couple stress has actually two reasons. The first is that he was possibly its introducer, or at least one of its main disseminators [416, 417]. The second is that this association will be helpful to distinguish this standard concept of couple stress from other less orthodox correlates, which will be introduced later on.

In the equations above, $R = a\sqrt{2/5}$ denotes the radius of gyration of a sphere (of radius a, see text below (2.7)) and $\boldsymbol{S}^{\mathfrak{g}}$ represents the relative spin velocity (compare with (2.6)–(2.9))

$$\boldsymbol{S}^{\mathfrak{g}} = \boldsymbol{s}^{\mathfrak{g}} - \boldsymbol{s} \ . \tag{2.38}$$

Combining (2.36) and (2.37), there arises thence the homogenized couple stress of the aggregate (for the definitions of the involved quantities, see (2.15)–(2.18))

$$\mathbf{m}(\boldsymbol{x},t) = \frac{1}{N_{\mathcal{R}}} \sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}} \left[\frac{a^2}{V^{\mathfrak{g}}} \sum_{\mathfrak{k}=1}^{K^{\mathfrak{g}}} \left(\boldsymbol{F}^{\mathfrak{g}\mathfrak{k}} \times \boldsymbol{k}^{\mathfrak{g}\mathfrak{k}} \right) \otimes \boldsymbol{k}^{\mathfrak{g}\mathfrak{k}} \right] - \varrho R^2 \left(\frac{1}{N_{\mathcal{R}}} \sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}} \boldsymbol{S}^{\mathfrak{g}} \otimes \boldsymbol{C}^{\mathfrak{g}} \right) \ . \tag{2.39}$$

Equation (2.39) can be interpreted as follows: in the first term, the quantity $\left(\boldsymbol{F}^{\mathfrak{g}\mathfrak{k}} \times \boldsymbol{k}^{\mathfrak{g}\mathfrak{k}} \right) a / V^{\mathfrak{g}}$ represents an angular impulse rate, i.e., the amount of spin (per unit volume) transferred per unit time along a distance a from the $\mathfrak{k}$-th contact to the center of mass of the $\mathfrak{g}$-th grain. On the other hand, the second term is associated to the transport of relative spin $\varrho R^2 \boldsymbol{S}^{\mathfrak{g}}$, which diffuses at velocity $\boldsymbol{C}^{\mathfrak{g}}$.

To conclude the set of general definitions of homogenized fields in granular media, which already include (1.1), (1.3), (1.7), (2.4), (2.10) and (2.20), it is now appropriate to issue the following *general definition of homogenized couple stress*

$$\mathbf{m}(\boldsymbol{x},t) \ = \ \frac{1}{V_{\mathcal{R}}} \int_{\mathcal{R}} \left(\mathbf{m}_{\mathtt{D}} - \gamma_{\mathtt{D}} \boldsymbol{\sigma}_{\mathtt{D}} \otimes \boldsymbol{C}_{\mathtt{D}} \right) \, \mathrm{d}^3 r \ , \tag{2.40}$$

which (as in the former case of stress) is based on the universal definition of non-convective flux (3.15). In (2.40), $\mathbf{m}_{\mathtt{D}}$ denotes the *conductive couple stress distribution*, while the other fields have been described in (1.7), (2.10) and (2.21).

The proof that (2.39) is a particularization of (2.40) follows the same lines as in the case of the Cauchy stress (see (2.20)–(2.33)). Firstly, the *relative spin distribution* is introduced (cf. (2.10))

$$\boldsymbol{\Sigma}_{\mathtt{D}} = \nu_{\mathtt{D}} \left(\boldsymbol{\sigma}_{\mathtt{D}} - \boldsymbol{\sigma} \right) \ , \tag{2.41}$$

enabling one to derive the identities

$$\int_{\mathcal{R}} \gamma_{\mathtt{D}} \boldsymbol{\Sigma}_{\mathtt{D}} \, \mathrm{d}^3 r = \mathbf{0} \ , \qquad \text{and} \qquad \int_{\mathcal{R}} \gamma_{\mathtt{D}} \boldsymbol{\sigma}_{\mathtt{D}} \otimes \boldsymbol{C}_{\mathtt{D}} \, \mathrm{d}^3 r \ = \int_{\mathcal{R}} \gamma_{\mathtt{D}} \boldsymbol{\Sigma}_{\mathtt{D}} \otimes \boldsymbol{C}_{\mathtt{D}} \, \mathrm{d}^3 r \ . \tag{2.42}$$

Then, the integrand of (2.40) is decomposed into individual granular contributions $\mathbf{m}_{\mathtt{D}}^{\mathfrak{g}}$, $\gamma_{\mathtt{D}}^{\mathfrak{g}}$, $\boldsymbol{C}_{\mathtt{D}}^{\mathfrak{g}}$ and $\boldsymbol{\Sigma}_{\mathtt{D}}^{\mathfrak{g}} = \nu_{\mathtt{D}}^{\mathfrak{g}} \left(\boldsymbol{\sigma}_{\mathtt{D}}^{\mathfrak{g}} - \boldsymbol{\sigma} \right)$, which vanish outside their ascribed grains (cf. (2.24)), leading to

$$\mathbf{m}(\boldsymbol{x},t) \ = \ \frac{1}{V_{\mathcal{R}}} \int_{\mathcal{R}} \sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}} \left(\mathbf{m}_{\mathtt{D}}^{\mathfrak{g}} - \gamma_{\mathtt{D}}^{\mathfrak{g}} \boldsymbol{\Sigma}_{\mathtt{D}}^{\mathfrak{g}} \otimes \boldsymbol{C}_{\mathtt{D}}^{\mathfrak{g}} \right) \, \mathrm{d}^3 r \ . \tag{2.43}$$

After interchange of the order of summation and integration in (2.43), one obtains (with the aid of (1.6), (1.7), $\varrho^{\mathfrak{g}} = \gamma^{\mathfrak{g}} = \gamma$ and $\boldsymbol{\Sigma}^{\mathfrak{g}} = R^2 \boldsymbol{S}^{\mathfrak{g}}$)

$$\mathbf{m}(\boldsymbol{x},t) \;=\; \frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\mathbf{m}^{\mathfrak{g}} \;-\; \varrho R^2\left(\frac{1}{N_{\mathcal{R}}}\sum_{\mathfrak{g}=1}^{N_{\mathcal{R}}}\boldsymbol{S}^{\mathfrak{g}}\otimes\boldsymbol{C}^{\mathfrak{g}}\right)\;. \tag{2.44}$$

The granular couple stress $\mathbf{m}^{\mathfrak{g}}$ is now given by (compare with (2.26))

$$\mathbf{m}^{\mathfrak{g}} = \frac{1}{V^{\mathfrak{g}}}\int\limits_{\mathcal{R}}\left(\mathbf{m}_{\mathtt{D}}^{\mathfrak{g}} - \gamma_{\mathtt{D}}^{\mathfrak{g}}\boldsymbol{\Sigma}_{\mathtt{D}}^{\mathfrak{g}}\otimes\boldsymbol{C}_{\mathtt{D}}^{\mathfrak{g}}\right)\,\mathrm{d}^3r\;, \tag{2.45}$$

with $\boldsymbol{\Sigma}_{\mathtt{D}}^{\mathfrak{g}}$ denoting the relative spin of an interior point of the $\mathfrak{g}$-th grain with respect to its own spin, i.e.,

$$\boldsymbol{\Sigma}_{\mathtt{D}}^{\mathfrak{g}} = \nu_{\mathtt{D}}^{\mathfrak{g}}\left(\boldsymbol{\sigma}_{\mathtt{D}}^{\mathfrak{g}} - \boldsymbol{\sigma}^{\mathfrak{g}}\right) = \nu_{\mathtt{D}}^{\mathfrak{g}}\left(\boldsymbol{\Sigma}_{\mathtt{D}}^{\mathfrak{g}} - \boldsymbol{\Sigma}^{\mathfrak{g}}\right)\;. \tag{2.46}$$

Of course, for rigid grains it immediately follows that $\boldsymbol{\Sigma}_{\mathtt{D}}^{\mathfrak{g}} = \mathbf{0}$ and thence, using similar arguments as in the case of the stress (see (2.26)–(2.28)), the expression (2.45) reduces to

$$\mathbf{m}^{\mathfrak{g}} = \frac{1}{V^{\mathfrak{g}}}\int\limits_{\mathcal{G}^{\mathfrak{g}}}\mathbf{m}_{\mathtt{D}}^{\mathfrak{g}}\,\mathrm{d}^3l\;. \tag{2.47}$$

Guided by the same reasoning as in (2.29)–(2.32), (with an appropriate substitution of $\mathbf{t}_{\mathtt{D}}^{\mathfrak{g}}$ by $\mathbf{m}_{\mathtt{D}}^{\mathfrak{g}}$) one can rewrite (2.47) as

$$\mathbf{m}^{\mathfrak{g}} = \frac{1}{V^{\mathfrak{g}}}\oint\limits_{\partial\mathcal{G}^{\mathfrak{g}}}(\mathbf{m}_{\mathtt{D}}^{\mathfrak{g}}\boldsymbol{e})\otimes\boldsymbol{l}^{\mathfrak{g}}\,\mathrm{d}^2l\;. \tag{2.48}$$

The term $\mathbf{m}_{\mathtt{D}}^{\mathfrak{g}}\boldsymbol{e}$ represents a couple stress vector field, acting on the $K^{\mathfrak{g}}$ contact points $\boldsymbol{l}^{\mathfrak{g}} = a\boldsymbol{k}^{\mathfrak{g}\mathfrak{k}}$ ($\mathfrak{k}=1,2,\ldots,K^{\mathfrak{g}}$) lying on the surface $\partial\mathcal{G}^{\mathfrak{g}}$ of the $\mathfrak{g}$-th grain. In principle, one could think of two fundamental types of couple stress vectors: those which are parallel and orthogonal, respectively, to the contact surface normal vector $\boldsymbol{e}$. For soft, deformable grains, both types may be effective in the transmission of spin from one granule to another, because the contact surface area is reasonably large. In contrast, for hard spheres, in which the contacts have infinitesimal surface areas $(\delta^2 l)^{\mathfrak{k}}$, only the components of the couple stress vectors lying on the plane of contact may play a significant role in the spin transmission, since couple stress vectors in the normal direction should depend strongly on the size of the contact surface, which is in this case negligibly small. Therefore, assuming for simplicity that the applied couple stress is uniform over the contacts, one can finally transform (2.32) into the sum

$$\mathbf{m}^{\mathfrak{g}} = \frac{a^2}{V^{\mathfrak{g}}}\sum_{\mathfrak{k}=1}^{K^{\mathfrak{g}}}\left(\boldsymbol{F}^{\mathfrak{g}\mathfrak{k}}\times\boldsymbol{k}^{\mathfrak{g}\mathfrak{k}}\right)\otimes\boldsymbol{k}^{\mathfrak{g}\mathfrak{k}}\;, \tag{2.49}$$

where $\boldsymbol{F}^{\mathfrak{g}\mathfrak{k}}\times\boldsymbol{k}^{\mathfrak{g}\mathfrak{k}} = (\mathbf{m}_{\mathtt{D}}^{\mathfrak{g}}\boldsymbol{e})(\delta^2 l)^{\mathfrak{k}}$ represents the couple acting on the $\mathfrak{k}$-th contact of the $\mathfrak{g}$-th grain. Thus, by combining (2.49) with (2.44), the particular relation (2.39) is recovered.

3. Chemically Reacting Mixtures of Polar Continua

Chemistry is that branch of natural philosophy in which the greatest improvements have been and may be made: it is on that account that I have made it my peculiar study; but at the same time I have not neglected the other branches of science. A man would make but a very sorry chemist if he attended to that department of human knowledge alone. If your wish is to become really a man of science, and not merely a petty experimentalist, I should advise you to apply to every branch of natural philosophy, including mathematics.

Mary Shelley (character: M. Waldman), [378] pp. 41–42

The theory of polar media has its origins in the work of Eugène Maurice Pierre Cosserat and his brother François [79], who introduced what is nowadays known as the *Cosserat medium*, which can be roughly envisaged as a region of space filled with triads of vectors[1]. For polar media, such vector triads are assumed rigid and, whereas their orientations are unimportant, their rotational motion gives rise to an additional dynamic field of intrinsic angular momentum called *spin*. While the theory of single component polar media is firmly established [15, 80–82, 87, 125, 133, 268], only very seldom have polar mixtures been object of study. This Chapter sets forth the state of art of this subject.

3.1 Synopsis and fundamentals

But however, I think I may preſume, that what I have hitherto diſcourſed, will induce you to think, that chymiſts have been much more happy in finding experiments than the cauſes of them; or in aſſigning the principles, by which they may beſt be explained. And indeed, when in the writings of *Paracelſus* I meet with ſuch phantaſtic and unintelligible diſcourſes, as that writer often puzzles and tires his reader with, fathered upon ſuch excellent experiments, as though he ſeldom clearly teaches, I often find he knew; methinks the chymiſts, in their ſearches after truth, are not unlike the navigators of *Solomon*'s *Tarſhiſh* fleet, who brought home from their long and tedious voyages, not only gold, and ſilver, and ivory, but apes and peacocks too: for ſo the writings of ſeveral (for I ſay not, all) of your hermetic philoſophers preſent us, together with divers ſubſtantial and noble experiments, theories, which either like

[1] In spite of the countless references to the treatise of Cosserat brothers [79], just few experts actually read it, owing to its cumbersome notation. A reperusal of their work in the light of a modern mathematical language is offered by Badur & Stumpf [21]. See also the presentation by Truesdell & Toupin [409].

peacocks feathers make a great ſhew, but are neither ſolid nor uſeful; or elſe like apes, if they have ſome appearance of being rational, are blemiſhed with ſome abſurdity or other, that, when they are attentively conſidered, make them appear ridiculous.

With these words Robert Boyle closes his celebrated work *The Sceptical Chymist* [53], which through its critics to spagyrists and peripatetics has established forth a new way of thinking chemistry towards the end of the 17th century. The scepticism of Boyle was basically in relation to the ancient attempts to identify the fundamental chemical elements by pure reasoning. Instead, he defended during his whole life the necessity of experiments for judicious scientific investigations.

Boyle's appeals were decades later personified in another scientist, who recognized since the very beginning of his scientific career the value of accurate measurements: his name was Antoine Laurent Lavoisier. Among Lavoisier's legacies (see e.g. [13]), the most consequential is with no doubts the statement that mass is never created or destroyed, but is merely shifted from one substance to another, a statement nowadays known as the *law of conservation of mass* – one of the cornerstones of modern continuum theory, as will be shown later on.

From the viewpoint of phenomenological–continuum approaches, the origins of the modern theory of mixtures are habitually traced back to Adolf Fick [138], who proposed in 1855 his celebrated laws of diffusion. He seems also to have been one of the first authors who formally envisaged a binary mixture as a superposition of continua – the same basic picture adopted in contemporary approaches to mixed continuous media. Fick's laws have been generalized in a early continuum theory of mixtures by Jozef Stefan [390]. Further attempts at more comprehensive theories of mixtures have been given by Pierre Duhem, Osborne Reynolds and Erwin Lohr, among others (see [409]). In particular, a system of balance equations for mixtures encompassing also chemical reactions and electromagnetic effects has been proposed in 1911 by Gustav Andreas J. Jaumann [230].

The modern program of the continuum thermodynamics of chemical mixtures effectively started during the Second World War with a paper by Eckart [115], in which he introduces the so-called *thermodynamics of irreversible processes*. This approach was later improved by Meixner, Onsager, Prigogine, Mazur and de Groot, among others (see [93, 209, 356, 409]), but it was soon overcome by the current *rational thermodynamics*. As a matter of fact, the ultimate forms of the balance equations of mass, linear momentum and energy for a mixture without microstructure – proposed within the frames of rational thermodynamics – are due to Truesdell [405]. Later, these equations have been generalized by Kelly [240], who added electromagnetic effects and introduced a *master balance equation* for the constituents, from which individual balance equations could be derived. Furthermore, he considered also the occurrence of spins and couple stresses, but unfortunately solely in supplementary balance equations for the angular momenta of the constituents: the kinetic energies of spins and powers of couple stresses have been left subsumed into the definitions of constituent internal energy and heat flux, respectively.

In spite of the efforts to achieve an utter thermodynamic theory of (structureless) mixtures, capable of generating sounding constitutive models [50, 124, 178], it was only with the work of Müller [315] that this objective was finally attained (see also [316]; a historical survey is available in [14]). On the other hand, attempts to construct general theories of mixtures which fully account for microstructural effects of polar media (i.e., in both, spin and energy balance equations) have been proposed by Allen & Kline [7] and Twiss & Eringen [411] – both suffering, nevertheless, from sensible deficiencies, as recently pointed out by Faria & Hutter [132]. The approach to mixtures of polar media discussed in the present Chapter follows the scheme discussed in this last cited work[2].

Effectively, following the assertion of Truesdell [407], the continuum theory of mixtures will be regarded here so as to describe the phenomena of diffusion, dissociation, combination, transformation and interaction of the constituents in their broadest sense. Mathematically, a mixture is defined as a superposition of N continuous bodies $\mathcal{B}^\alpha$ ($\alpha = 1, 2, \ldots, N$), all able to occupy simultaneously the same region of space. Consequently, in order to refer to any particle of some constituent of this continuum, at a given time t, it is necessary to identify not only the current position x_i of the respective particle, but also its *constituent label* α. Accordingly, the mass density of the component α at the position x_i and time t is given by $\varrho^\alpha(x_i, t)$, while the mass density of the mixture $\varrho(x_i, t)$ is defined by

$$\varrho = \sum_{\alpha=1}^{N} \varrho^\alpha \, . \tag{3.1}$$

Its translational velocity field is $v_i(x_j, t)$, and it can be readily computed from the velocities $v_i^\alpha(x_j, t)$ assigned to the distinct chemical constituents $\alpha = 1, 2, \ldots, N$ by recalling the additivity of mass and linear momentum, viz.

$$v_i = \frac{1}{\varrho} \sum_{\alpha=1}^{N} \varrho^\alpha v_i^\alpha \, . \tag{3.2}$$

Hence, $v_i(x_j, t)$ is the barycentric velocity of the mixture. Moreover, it follows that the relative (diffusive) velocity of the constituent α reads

$$C_i^\alpha = v_i^\alpha - v_i \, . \tag{3.3}$$

3.2 Convective, diffusive and conductive fluxes

Of great significance is the recognition of the different types of fluxes in a heterogeneous continuum. For an easier understanding, this will be done heuristically in this section.

[2] Condiff & Brenner [78] and Dunwoody [109] have also put forward alternative theories of microstructured mixtures, but in somewhat different contexts. Owing to their peculiarities, these theories will be considered in Chaps. 4 and 6.

Let $\mathcal{W}$ denote a (piecewise) smooth oriented surface moving with velocity $v_i^{\mathcal{W}}(x_j, t)$ within a region $\mathcal{V} \subset \mathcal{B}$. In the simplest instance, when all thermodynamic fields are continuous through the surface, the mass flux across $\mathcal{W}$, for any particular chemical constituent α, can be easily derived from the expressions

$$J^{\alpha}(\mathcal{W}, t) = \int_{\mathcal{W}} j_i^{\alpha} e_i^{\mathcal{W}} \, \mathrm{d}^2 x \ , \tag{3.4}$$

where $e_i^{\mathcal{W}}$ denotes the unit vector normal to $\mathcal{W}$ and

$$j_i^{\alpha}(x_j, t\,; v_k^{\mathcal{W}}) = \varrho^{\alpha} \left(v_i^{\alpha} - v_i^{\mathcal{W}} \right) \tag{3.5}$$

is the mass flux density for the chemical constituent α. Hence, besides x_i and t, the flux j_i^{α} depends also on the parameters $v_k^{\mathcal{W}}$, which specify the motion of the surface $\mathcal{W}$. Concerning this, there are two particular choices of $v_i^{\mathcal{W}}$ which deserve special interest:

a) $v_i^{\mathcal{W}} = 0$ the surface is at rest and the flux is called *convective*[3]. Equation (3.5) reads then $j_i^{\alpha}(x_j, t\,; 0) = \varrho^{\alpha} v_i^{\alpha}$.

b) $v_i^{\mathcal{W}} = v_i$ the surface accompanies the (barycentric) motion of the mixture, and it is in this sense called a *material surface*. Equation (3.5) reduces in this case to $j_i^{\alpha}(x_j, t) = \varrho^{\alpha} C_i^{\alpha}$ and the flux is called *diffusive*.

In particular, when Situation (b) is considered with $C_i^{\alpha} = 0$ ($\forall\ \alpha$), then there is no mass flux at all and $\mathcal{W}$ is called an *impermeable* or *material wall*. Of course, for single media – where no diffusion takes place – any material surface is also a material wall (a typical example is the boundary of a solid). Additionally, one could also choose $v_i^{\mathcal{W}}$ equal to the velocity of some chemical constituents, allowing so a selective flux of species. Such a moving surface is called a *semi-permeable wall*.

The results above can be easily extended to compute the flux of any additive property A besides mass, be it scalar, vector or tensor valued, provided one recognizes that transfers *without net mass transport* across the surface can also occur, viz. through *conductive fluxes*. Effectively, the flux of A across $\mathcal{W}$, for any particular constituent α, can be calculated from

$$\mathsf{F}^{\alpha}(\mathcal{W}, t) = \int_{\mathcal{W}} \left(\mathsf{q}_i^{\alpha} + \mathsf{f}_i^{\alpha} \right) e_i^{\mathcal{W}} \, \mathrm{d}^2 x \ , \tag{3.6}$$

where

$$\mathsf{f}_i^{\alpha}(x_j, t;\, v_k^{\mathcal{W}}) = \varrho^{\alpha} \mathsf{a}^{\alpha} \left(v_i^{\alpha} - v_i^{\mathcal{W}} \right) \ . \tag{3.7}$$

In (3.6) and (3.7), $\varrho^{\alpha} \mathsf{a}^{\alpha}$ denotes the density field of A^{α}, while q_i^{α} is its correspondent *conductive flux density*[4]. Of course, the expression for the mass flux (3.4) may be

[3] Of course, the concept of "convective flux" is to some extent flexible. For instance, with respect to the moving surface $\mathcal{W}$, it could be said that the mass flux density j_i^{α} is invariably convective. Nevertheless, in this chapter convection will be always considered in connection with the motion of the medium with respect to a "fixed" observer (reference frame).

[4] The sense of "density" attributed to q_i^{α} is important in order to distinguish it from F^{α}. In the literature, however, it is common to call q_i^{α} simply "flux", for brevity. This abridgement will be adopted also here, except when the distinction between q_i^{α} and F^{α} requires the contrary.

recovered by simply setting $\mathsf{a}^{\alpha} = 1$ in (3.7) and $\mathsf{q}_i^{\alpha} = 0$ in (3.6) (the latter arising from the fact that mass transfer without mass transport is something nonsensical). Moreover, as to the relation (3.7), the definitions presented in Situations (a) and (b) remain valid. In particular, Situation (b) is of conspicuous interest, since diffusion is a fundamental feature of any mixture, deserving therefore special attention.

Basing on this reasoning, it seems appropriate to concentrate attention, until the end of this Section, exclusively on the case in which the already introduced surface $\mathcal{W}$ is a material surface. In such an instance, there follows from (3.6) and (3.7) that the flux of the additive quantity A^{α} is given by

$$\mathsf{F}^{\alpha}(\mathcal{W},t) = \int_{\mathcal{W}} (\mathsf{q}_i^{\alpha} + \varrho^{\alpha}\mathsf{a}^{\alpha}C_i^{\alpha})\, \mathrm{e}_i^{\mathcal{W}}\, \mathrm{d}^2x \;, \tag{3.8}$$

being clearly composed of conductive (q_i^{α}) and diffusive ($\varrho^{\alpha}\mathsf{a}^{\alpha}C_i^{\alpha}$) parts. Physically, the flux F^{α} defines the amount of A^{α} which is transferred across the surface $\mathcal{W}$ per unit time. Now, as far as the constituent quantity A^{α} is additive, the mixture quantity A should be given by the sum, over all α, of A^{α}. Accordingly, the mixture flux F should then be given by

$$\begin{aligned}
\mathsf{F} = \sum_{\alpha=1}^{N} \mathsf{F}^{\alpha} &= \sum_{\alpha=1}^{N} \int_{\mathcal{W}} (\mathsf{q}_i^{\alpha} + \varrho^{\alpha}\mathsf{a}^{\alpha}C_i^{\alpha})\, \mathrm{e}_i^{\mathcal{W}}\, \mathrm{d}^2x \\
&= \int_{\mathcal{W}} \sum_{\alpha=1}^{N} (\mathsf{q}_i^{\alpha} + \varrho^{\alpha}\mathsf{a}^{\alpha}C_i^{\alpha})\, \mathrm{e}_i^{\mathcal{W}}\, \mathrm{d}^2x \\
&= \int_{\mathcal{W}} \mathsf{q}_i \mathrm{e}_i^{\mathcal{W}}\, \mathrm{d}^2x \;,
\end{aligned} \tag{3.9}$$

where

$$\mathsf{q}_i = \sum_{\alpha=1}^{N} (\mathsf{q}_i^{\alpha} + \varrho^{\alpha}\mathsf{a}^{\alpha}C_i^{\alpha}) \tag{3.10}$$

defines the *conducive flux density* of the mixture quantity A. Indeed, by setting $\mathsf{a}^{\alpha} = 1$ and $\mathsf{q}_i^{\alpha} = 0$ in (3.10), there follows from (3.2) that $\mathsf{q}_i = 0$, as should be for a conductive flux[5]. Finally, recalling the additivity of A^{α}, one can define

$$\mathsf{D}^{\alpha} = \mathsf{a}^{\alpha} - \mathsf{a} \qquad \text{where} \qquad \mathsf{a} = \frac{1}{\varrho}\sum_{\alpha=1}^{N} \varrho^{\alpha}\mathsf{a}^{\alpha} \;, \tag{3.11}$$

enabling one to rewrite (3.10) as

$$\mathsf{q}_i = \sum_{\alpha=1}^{N} (\mathsf{q}_i^{\alpha} + \varrho^{\alpha}\mathsf{D}^{\alpha}C_i^{\alpha}) \;. \tag{3.12}$$

[5]Evidently, since diffusion is defined with respect to the mixture motion, there is no logic in speaking about a "mixture diffusive flux".

It must be emphasized that the definition (3.10) (or alternatively (3.12)) is quite comprehensive, being valid for any additive property A, provided that (3.11) holds. In this sense, it is called the *generic definition of conductive flux density in a mixture*. Further, A might be a tensor of any rank: if e.g. it has rank two (say), then its density is denoted by $\varrho \mathsf{a}_{jk}$ and its conductive flux density by q_{ijk}.

The whole discussion on fluxes carried on up to now has been based on the fundamental assumption that all constituents of the mixture may occupy simultaneously the same region of space – a kind of metaphorical superposition of matter. However, in some situations (e.g. in heterogeneous or immiscible mixtures) it might be advantageous to get more insight into the structure of the mixture by relaxing such a metaphor of interpenetrating matter. This can be accomplished by assuming that a material point (i.e., a particle of the mixture) is in fact not a geometrical point, but rather a very small representative elementary volume (REV) of the mixture (cf. Sect. 1.2). Effectively, let the mentioned REV occupy a region $\mathcal{R}$ of space, which has volume $V_{\mathcal{R}}$ and is momentarily embedded within the mixture. If the fraction of $V_{\mathcal{R}}$ which is instantaneously occupied by the constituent α is $V_{\mathcal{R}}^{\alpha}/V_{\mathcal{R}}$, then one can introduce the definitions

$$\gamma^{\alpha} = \frac{V_{\mathcal{R}}}{V_{\mathcal{R}}^{\alpha}} \varrho^{\alpha} \ , \qquad \text{and} \qquad \mathsf{Q}_{i}^{\alpha} = \frac{V_{\mathcal{R}}}{V_{\mathcal{R}}^{\alpha}} \mathsf{q}_{i}^{\alpha} \ . \tag{3.13}$$

The first expression is called the *true mass density* of constituent α (cf. Sect. 1.3), while the second one can be interpreted as the conductive flux of the true density of A^{α}, viz. $\gamma^{\alpha}\mathsf{a}^{\alpha}$. Inserting these definitions into (3.10), one derives

$$\mathsf{q}_{i} = \frac{1}{V_{\mathcal{R}}} \sum_{\alpha=1}^{N} \left(\mathsf{Q}_{i}^{\alpha} + \gamma^{\alpha} \mathsf{a}^{\alpha} C_{i}^{\alpha} \right) V_{\mathcal{R}}^{\alpha} \ . \tag{3.14}$$

Whereas (3.14) is instructive by itself, its real potential is revealed when the number (and/or character) of constituents in a mixture is beforehand unknown. In this case, one might divide the region $\mathcal{R}$ in a huge number of microscopic cells, and consider each of them as filled with a distinct hypothetical chemical constituent. Since the precision of this description depends on the niceties of this lattice of cells, it would be preferable to make them infinitesimally small, each one located at a microscopic point r_i within the REV. Consequently, in the limit of infinitesimal cells, $V_{\mathcal{R}}^{\alpha}$ becomes a microscopic volume element $\mathrm{d}^3 r$, while the number of constituents N increases dramatically. But since every cell is now related to an individual constituent of the mixture, it follows that constituents may be identified by the cellular microscopic position r_i, instead of the label α, in such a way that the fields Q_{i}^{α}, γ^{α}, a^{α} and C_{i}^{α} (all functions of x_j and t) transform into the distributions $\mathsf{Q}_{\mathtt{D}i}$, $\gamma_{\mathtt{D}}$, $\mathsf{a}_{\mathtt{D}}$ and $C_{\mathtt{D}i}$ (all functions of x_j, t and r_k). Under such conditions, the sum (3.14) becomes an integral over all cells of the form

$$\mathsf{q}_{i} \ = \ \frac{1}{V_{\mathcal{R}}} \int\limits_{\mathcal{R}} \left(\mathsf{Q}_{\mathtt{D}i} + \gamma_{\mathtt{D}} \mathsf{a}_{\mathtt{D}} C_{\mathtt{D}i} \right) \mathrm{d}^3 r \ . \tag{3.15}$$

This is the version of the generic definition of flux density which is employed in the homogenization of stresses and couple stresses discussed in Chap. 2. Evidently, for known distribution of chemical constituents, (3.15) reduces to (3.14), which in turn is equivalent to (3.10).

3.3 Master balance equations and jump conditions

In continuum theory, fields are assumed to be smooth almost everywhere. By "almost everywhere" it is meant that a finite number of point, line and surface singularities (usually involving discontinuity jumps in the values of some fields) are permitted within the medium. Points of a medium in which no singularities arise are called *regular*, and singular otherwise.

Regular points. Consider a region $\mathcal{V} \subset \mathbb{R}^3$ fixed in space, with piecewise smooth boundary $\partial\mathcal{V}$. Assume also that, for the time interval of interest, $\mathcal{V} \subseteq \mathcal{B}$. As far as the region $\mathcal{V}$ is fixed in $\mathbb{R}^3$, it follows that its boundary is at rest, and that mass fluxes across $\partial\mathcal{V}$ are convective (Situation (a), Sect. 3.2).

If there are no singularities in $\mathcal{V}$, all points within that region are regular, and the standard axiom of balance for a regular region applies, asserting that the time rate of an arbitrary additive property in $\mathcal{V}$ is balanced by its production inside the region and supplies from outside [290, 317]. Moreover, depending on their causes, such supplies can be classified as fluxes from the neighborhood across the boundaries of $\mathcal{V}$, or volume interactions with external sources (e.g., due to gravitational and electromagnetic fields). Thence, from the arguments above and the results of Sect. 3.2, one can write for every constituent α of the mixture the following *global master balance equation* (*for regions without singularities*)

$$\underbrace{\int_{\mathcal{V}} \frac{\partial \varrho^\alpha \mathsf{a}^\alpha}{\partial t}\,\mathrm{d}^3x}_{\mathrm{d}A^\alpha/\mathrm{d}t} = \underbrace{\int_{\mathcal{V}} \varrho^\alpha \mathsf{p}^\alpha\,\mathrm{d}^3x}_{\text{production}} - \underbrace{\int_{\partial\mathcal{V}} (\mathsf{q}_i^\alpha + \varrho^\alpha \mathsf{a}^\alpha v_i^\alpha)\, e_i^\nu\,\mathrm{d}^2x}_{\text{conductive \& convective flux } F^\alpha} + \underbrace{\int_{\mathcal{V}} \varrho^\alpha \mathsf{s}^\alpha\,\mathrm{d}^3x}_{\text{volume supply}}\,, \quad (3.16)$$

where use was made of the fact that $\mathcal{V}$ is fixed in space and free of singularities, which implies the identities (cf. (3.6) and (3.7))

$$\frac{\mathrm{d}}{\mathrm{d}t} A^\alpha(t) = \frac{\mathrm{d}}{\mathrm{d}t} \int_{\mathcal{V}} \varrho^\alpha \mathsf{a}^\alpha\,\mathrm{d}^3x = \int_{\mathcal{V}} \frac{\partial}{\partial t}(\varrho^\alpha \mathsf{a}^\alpha)\,\mathrm{d}^3x\,, \qquad \mathsf{f}_i^\alpha = \varrho^\alpha \mathsf{a}^\alpha v_i^\alpha\,. \quad (3.17)$$

In (3.16) and (3.17), $\varrho^\alpha \mathsf{a}^\alpha$ is the density field of the arbitrary additive quantity A^α and the specific quantities p^α and s^α denote its production and volume supply, respectively, while q_i^α is its conductive flux density. Moreover, e_i^ν denotes the unit vector normal to $\partial\mathcal{V}$. Finally, from Gauss' theorem [1]

$$\int_{\partial\mathcal{V}} (\mathsf{q}_i^\alpha + \varrho^\alpha \mathsf{a}^\alpha v_i^\alpha)\, e_i^\nu\,\mathrm{d}^2x = \int_{\mathcal{V}} \frac{\partial}{\partial x_i}(\mathsf{q}_i^\alpha + \varrho^\alpha \mathsf{a}^\alpha v_i^\alpha)\,\mathrm{d}^3x\,, \quad (3.18)$$

and thence, since the region $\mathcal{V}$ is arbitrary and the integrands are smooth, there follows from (3.16)–(3.18) the *local master balance equation*

$$\frac{\partial \varrho^\alpha \mathsf{a}^\alpha}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^\alpha \mathsf{a}^\alpha v_i^\alpha + \mathsf{q}_i^\alpha\right) = \varrho^\alpha \mathsf{p}^\alpha + \varrho^\alpha \mathsf{s}^\alpha . \tag{3.19}$$

Singular points. Up to now, only surfaces in $\mathcal{B}$ which do not affect the continuity of the thermodynamic fields within the body have been considered. Notwithstanding, most natural surfaces generate field disturbances, often in the form of jump discontinuities. Examples include boundaries of any type, shock and acceleration waves, etc., which are all collectively named *singular surfaces*. In such cases, the analysis of fluxes presented in Sect. 3.2 must be revised by relaxing the continuity condition, i.e., by assuming that all thermodynamic fields are smooth on both sides of $\mathcal{W}$ but they can suffer jump discontinuities across it. In this situation, the singular surface $\mathcal{W}$ divides $\mathcal{V}$ in two subregions, viz. $\mathcal{V}^+$ and $\mathcal{V}^-$, with $e_i^{\mathcal{W}}$ pointing into $\mathcal{V}^+$ (Fig. 3.1).

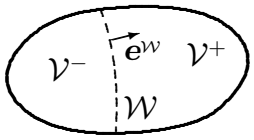


Fig. 3.1. Two-dimensional sketch of the region $\mathcal{V}$, which is divided by a moving singular surface $\mathcal{W}$ (dashed line) in two parts, viz. $\mathcal{V}^-$ and $\mathcal{V}^+$. The unit vector $e_i^{\mathcal{W}}$, normal to the moving surface, is also shown.

For any field U, the limits U^+ and U^- taken from each side of $\mathcal{W}$ are not necessarily the same, and their difference

$$[\![\, \mathsf{U} \,]\!] = \mathsf{U}^+ - \mathsf{U}^- , \tag{3.20}$$

which is a smooth field on $\mathcal{W}$ by assumption, defines the *jump* of U across the singular surface. Consequently, in order to have a balance between the total influx and outflux of the additive quantity A in $\mathcal{W}$, one must admit the possibility that the singular surface acts as a source (or sink) of A. Hence, from (3.6) and (3.20) follows

$$[\![\, \mathsf{F}^\alpha \,]\!] = \int_{\mathcal{W}} [\![\, \mathsf{q}_i^\alpha + \mathsf{f}_i^\alpha \,]\!] e_i^{\mathcal{W}} \, \mathrm{d}^2 x = \int_{\mathcal{W}} (\mathsf{b}^\alpha + \mathsf{z}^\alpha) \, \mathrm{d}^2 x, \tag{3.21}$$

where the surface densities of balance b^α and of external supply z^α are both defined as smooth functions on $\mathcal{W}$. Finally, from the assumed smoothness of the integrands appearing in (3.21), it can be concluded that, at each point of the singular surface, the *master jump conditions*

$$[\![\, \mathsf{q}_i^\alpha + \varrho^\alpha \mathsf{a}^\alpha (v_i^\alpha - v_i^{\mathcal{W}}) \,]\!] e_i^{\mathcal{W}} = \mathsf{b}^\alpha + \mathsf{z}^\alpha \tag{3.22}$$

must hold.

It could also be shown (see for instance [221, 317]) that the surface density of balance b^α stems from a combination of topographic and material properties intrinsic to the singular surface, including curvature, surface stresses and fluxes. Nevertheless, such details go beyond the scope and necessities of this work. Indeed, it is sufficient to

remark here that, when the singular surface possesses intrinsic properties (allowing so $\mathsf{b}^{\alpha} \neq 0$ and $\mathsf{z}^{\alpha} \neq 0$), it is sometimes called a *thin shell* or *membrane*.

For completeness, we write down also the *global master balance equation for a region enclosing a moving singular surface*, viz.

$$\int_{\mathcal{V}} \frac{\partial \varrho^{\alpha} \mathsf{a}^{\alpha}}{\partial t} \, \mathrm{d}^3 x \; - \int_{\mathcal{W}} [\![\, \varrho^{\alpha} \mathsf{a}^{\alpha} \,]\!] v_i^{\mathcal{W}} e_i^{\mathcal{W}} \, \mathrm{d}^2 x$$
$$= \int_{\mathcal{V}} (\varrho^{\alpha} \mathsf{p}^{\alpha} + \varrho^{\alpha} \mathsf{s}^{\alpha}) \, \mathrm{d}^3 x \; - \int_{\partial \mathcal{V}} (\mathsf{q}_i^{\alpha} + \varrho^{\alpha} \mathsf{a}^{\alpha} v_i^{\alpha}) \, e_i^{\mathcal{V}} \, \mathrm{d}^2 x \; + \int_{\mathcal{W}} (\mathsf{b}^{\alpha} + \mathsf{z}^{\alpha}) \, \mathrm{d}^2 x \, . \quad (3.23)$$

The last integral in (3.23) introduces two obvious accretions to (3.16) due to the intrinsic properties of the singular surface $\mathcal{W}$ discussed above. They represent additional production and external supply terms, respectively. The second integral on the left-hand side of (3.23) is the appropriate correction of (3.17) when the region $\mathcal{V}$ is swept by a moving singular surface. Roughly, it is generated by the progressive swallowing of the frontal region $\mathcal{V}^{+}$ by the singular surface, which extracts an amount $[\![\, \varrho^{\alpha} \mathsf{a}^{\alpha} \,]\!]$ from the respective field, releasing the rest in the rear region $\mathcal{V}^{-}$. In other words, the time rate of the quantity A^{α} depends, in this case, also on the product of its jump across $\mathcal{W}$ with the volume swept by the singular surface per unit time. Of course, it is easy to infer from standard arguments [221, 290, 317] that (3.23) includes (3.16), (3.19), (3.21) and (3.22) as particular cases.

3.4 Constituent balance equations for polar media

One of the simplest conceivable types of microstructured continua is undoubtedly the polar medium. This is a suitable particularization of the theory of Cosserat continua, and is obtained through the assumption that microstructural effects manifest themselves solely via spin. Evidently, the monodisperse aggregate of spherical granules considered in Chap. 2 is a particular example of polar medium. What makes the theory of polar media specially tractable is the fact that spin has well known features and a definite balance equation, both derived from the general properties of angular momenta.

On the other hand, the substructure of usual chemical mixtures is characterized by the concept of superposing continua, discussed in Sect. 3.1. This yields in principle an increase of the number of fields describing mass, energy and motion by a factor N, where N denotes the number of constituents in the mixture.

By combining the above statements, one concludes that thermodynamic processes involving motion with mass and energy exchanges in chemical mixtures of polar media should be essentially characterized by the knowledge of N constituent fields of $(\alpha = 1, 2, \ldots, N)$

$$\begin{aligned} &\text{mass density} && \varrho^\alpha(x_i,t)\ ,\\ &\text{specific linear momentum (translational velocity)} && v_i^\alpha(x_j,t)\ ,\\ &\text{specific spin} && \sigma_i^\alpha(x_j,t)\ ,\\ &\text{specific internal energy} && e^\alpha(x_i,t)\ , \end{aligned} \tag{3.24}$$

at every position x_i and time instant t. To determine these fields one disposes of the constituent balance equations of mass, momenta and energy, which can be derived from the master balance equations (3.19) and (3.22) as follows:

• mass

a^α	q_i^α	p^α	s^α	b^α	z^α
1	0	$\mathit{\Gamma}^\alpha$	0	${}^{\varrho}b^\alpha$	${}^{\varrho}z^\alpha$

$$\frac{\partial \varrho^\alpha}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^\alpha v_i^\alpha\right) = \varrho^\alpha \mathit{\Gamma}^\alpha\ , \tag{3.25}$$

$$\left[\!\left[\, \varrho^\alpha \left(v_i^\alpha - v_i^{\mathcal{W}}\right) \right]\!\right] e_i^{\mathcal{W}} = {}^{\varrho}b^\alpha + {}^{\varrho}z^\alpha\ , \tag{3.26}$$

• linear momentum

a^α	q_i^α	p^α	s^α	b^α	z^α
v_i^α	$-\mathsf{t}_{ij}^\alpha$	κ_i^α	g_i^α	${}^{v}b^\alpha$	${}^{v}z^\alpha$

$$\frac{\partial \varrho^\alpha v_i^\alpha}{\partial t} + \frac{\partial}{\partial x_j}\left(\varrho^\alpha v_i^\alpha v_j^\alpha - \mathsf{t}_{ij}^\alpha\right) = \varrho^\alpha \kappa_i^\alpha + \varrho^\alpha g_i^\alpha\ , \tag{3.27}$$

$$\left[\!\left[\, \varrho^\alpha v_i^\alpha \left(v_j^\alpha - v_j^{\mathcal{W}}\right) - \mathsf{t}_{ij}^\alpha \right]\!\right] e_j^{\mathcal{W}} = {}^{v}b_i^\alpha + {}^{v}z_i^\alpha\ , \tag{3.28}$$

• angular momentum (total)

a^α	q_i^α	p^α	s^α	b^α	z^α
L_i^α	$-\mathsf{M}_{ij}^\alpha$	N_i^α	K_i^α	${}^{L}b^\alpha$	${}^{L}z^\alpha$

$$\frac{\partial \varrho^\alpha L_i^\alpha}{\partial t} + \frac{\partial}{\partial x_j}\left(\varrho^\alpha L_i^\alpha v_j^\alpha - \mathsf{M}_{ij}^\alpha\right) = \varrho^\alpha N_i^\alpha + \varrho^\alpha K_i^\alpha\ , \tag{3.29}$$

$$\left[\!\left[\, \varrho^\alpha L_i^\alpha \left(v_j^\alpha - v_j^{\mathcal{W}}\right) - \mathsf{M}_{ij}^\alpha \right]\!\right] e_j^{\mathcal{W}} = {}^{L}b_i^\alpha + {}^{L}z_i^\alpha\ , \tag{3.30}$$

• energy (total)

a^α	q_i^α	p^α	s^α	b^α	z^α
E^α	Q_i^α	P^α	R^α	${}^{E}b^\alpha$	${}^{E}z^\alpha$

$$\frac{\partial \varrho^\alpha E^\alpha}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^\alpha E^\alpha v_i^\alpha + Q_i^\alpha\right) = \varrho^\alpha P^\alpha + \varrho^\alpha R^\alpha \,, \tag{3.31}$$

$$\left[\!\left[\, \varrho^\alpha E^\alpha \left(v_i^\alpha - v_i^{\mathcal{W}}\right) + Q_i^\alpha \,\right]\!\right] e_i^{\mathcal{W}} = {}^{E}b^\alpha + {}^{E}z^\alpha \,. \tag{3.32}$$

Furthermore, for later reference in the frames of thermodynamics and constitutive theories, it is useful to include in the list of basic balance equations also the one related to entropy, viz.

• entropy

a^α	q_i^α	p^α	s^α	b^α	z^α
η^α	ϕ_i^α	ς^α	s^α	${}^{\eta}b^\alpha$	${}^{\eta}z^\alpha$

$$\frac{\partial \varrho^\alpha \eta^\alpha}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^\alpha \eta^\alpha v_i^\alpha + \phi_i^\alpha\right) = \varrho^\alpha \varsigma^\alpha + \varrho^\alpha s^\alpha \,, \tag{3.33}$$

$$\left[\!\left[\, \varrho^\alpha \eta^\alpha \left(v_i^\alpha - v_i^{\mathcal{W}}\right) + \phi_i^\alpha \,\right]\!\right] e_i^{\mathcal{W}} = {}^{\eta}b^\alpha + {}^{\eta}z^\alpha \,. \tag{3.34}$$

In (3.25)–(3.34), the quantities ϱ^α, $\varrho^\alpha v_i^\alpha$, $\varrho^\alpha L_i^\alpha$, $\varrho^\alpha E^\alpha$, $\varrho^\alpha \eta^\alpha$ represent the densities of mass, linear and total angular momenta, total energy and entropy of the constituent α, with ${}^{\varrho}b^\alpha$, ${}^{v}b^\alpha$, ${}^{L}b^\alpha$, ${}^{E}b^\alpha$, ${}^{\eta}b^\alpha$ and ${}^{\varrho}z^\alpha$, ${}^{v}z^\alpha$, ${}^{L}z^\alpha$, ${}^{E}z^\alpha$, ${}^{\eta}z^\alpha$ being their respective surface densities of balance and of supply. Additionally, t_{ij}^α and M_{ij}^α denote the Cauchy stress and the total couple of stresses of the constituent α, Q_i^α and ϕ_i^α are the constituent fluxes of total energy and entropy, while Γ^α, κ_i^α, N_i^α and P^α stand for the chemical productions mass, momenta, and energy of the α-th constituent, respectively. The customary constituent fields of spin σ^α, internal energy ε^α, Voigt couple stress m_{ij}^α and heat flux q_i^α are related to L_i^α, E_i^α, M_{ij}^α and Q_i^α through the relations

$$L_i^\alpha = \epsilon_{ijk} x_j v_k^\alpha + \sigma_i^\alpha, \qquad \mathsf{M}_{il}^\alpha = \epsilon_{ijk} x_j \mathsf{t}_{kl}^\alpha + \mathsf{m}_{il}^\alpha, \tag{3.35}$$

$$E^\alpha = e^\alpha + \tfrac{1}{2} v_i^\alpha v_i^\alpha + \tfrac{1}{2}\sigma_i^\alpha s_i^\alpha, \qquad Q_j^\alpha = q_j^\alpha - \mathsf{t}_{ij}^\alpha v_i^\alpha - \mathsf{m}_{ij}^\alpha s_i^\alpha \,, \tag{3.36}$$

where s_i^α is the spin velocity of the constituent α, defined in terms of the constituent fields of specific spin σ_i^α and specific inertia tensor I_{ij}^α as (cf. (2.5))

$$\sigma_i^\alpha = \mathsf{I}_{ij}^\alpha s_j^\alpha \,, \qquad \text{with} \qquad \mathsf{I}_{ij}^\alpha = \mathsf{I}_{ji}^\alpha \,. \tag{3.37}$$

Moreover, the chemical productions of spin ν_i^α and internal energy ε^α, as well as the specific fields of body couple c_i^α and radiation r^α, are introduced through the relations

$$K_i^\alpha = \epsilon_{ijk} x_j g_k^\alpha + c_i^\alpha, \qquad N_i^\alpha = \epsilon_{ijk} x_j \kappa_k^\alpha + \nu_i^\alpha \ , \tag{3.38}$$

$$R^\alpha = r^\alpha + g_i^\alpha v_i^\alpha + c_i^\alpha s_i^\alpha, \qquad P^\alpha = \varepsilon^\alpha + \kappa_i^\alpha v_i^\alpha + \nu_i^\alpha s_i^\alpha, \tag{3.39}$$

which lead, with the aid of (3.25), (3.27), (3.29) and (3.37), to the *constituent balance equation of spin*

$$\frac{\partial \varrho^\alpha \sigma_i^\alpha}{\partial t} + \frac{\partial}{\partial x_j}\left(\varrho^\alpha \sigma_i^\alpha v_j^\alpha - \mathsf{m}_{ij}^\alpha\right) + \epsilon_{ijk}\mathsf{t}_{jk}^\alpha = \varrho^\alpha \nu_i^\alpha + \varrho^\alpha c_i^\alpha \ . \tag{3.40}$$

Equation (3.40) is in fact quite general and, in combination with (3.37), it may encompass complex microstructural effects by means of changes in the constituent inertia tensor I_{ij}^α. In order to avoid these complications, the existence of a material parameter is usually presupposed in the theory of polar media, namely the *effective radius of gyration* R^α, so that $\mathsf{I}_{ij}^\alpha = (R^\alpha)^2 \delta_{ij}$. Under such conditions, (3.40) reduces to a balance equation of spin velocity

$$\frac{\partial \varrho^\alpha (R^\alpha)^2 s_i^\alpha}{\partial t} + \frac{\partial}{\partial x_j}\left[\varrho^\alpha (R^\alpha)^2 s_i^\alpha v_j^\alpha - \mathsf{m}_{ij}^\alpha\right] + \epsilon_{ijk}\mathsf{t}_{jk}^\alpha = \varrho^\alpha \nu_i^\alpha + \varrho^\alpha c_i^\alpha \ , \tag{3.41}$$

and from (3.25), (3.27), (3.29), (3.31) and (3.35)–(3.39) there follows in this case the *constituent balance equation of internal energy*

$$\frac{\partial \varrho^\alpha e^\alpha}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^\alpha e^\alpha v_i^\alpha + q_i^\alpha\right) - \mathsf{t}_{ij}^\alpha \frac{\partial v_i^\alpha}{\partial x_j} - \mathsf{m}_{ij}^\alpha \frac{\partial s_i^\alpha}{\partial x_j} - \epsilon_{ijk} s_i^\alpha t_{jk}^\alpha = \varrho^\alpha \varepsilon^\alpha + \varrho^\alpha r^\alpha. \tag{3.42}$$

3.5 Conservation laws for microstructured mixtures

There remains now to derive the fields and balance equations for the mixture. As illustrated in Chap. 4, this might be a complicated task, specially in the case of microstructured mixtures in non-inertial frames. Therefore, for simplicity, only inertial reference frames are considered here, while the influence of inertial effects on the mixture behavior is analyzed in Chap. 4.

The starting point is of course the definitions of mass density and specific linear momentum (translational velocity) of the mixture, viz. (3.1) and (3.2). Actually, seeing that all the densities ϱ^α, $\varrho^\alpha v_i^\alpha$, $\varrho^\alpha L_i^\alpha$, $\varrho^\alpha E^\alpha$ and $\varrho^\alpha \eta^\alpha$ are additive and have been treated on the same footing in (3.25)–(3.34), there is no reason to refrain from embracing the simple definitions

$$L_i = \frac{1}{\varrho}\sum_{\alpha=1}^{N} \varrho^\alpha L_i^\alpha \ , \qquad E = \frac{1}{\varrho}\sum_{\alpha=1}^{N} \varrho^\alpha E^\alpha \ , \qquad \eta = \frac{1}{\varrho}\sum_{\alpha=1}^{N} \varrho^\alpha \eta^\alpha \ . \tag{3.43}$$

Once the relations above are adopted, it immediately follows from the generic definition of flux density (3.12) that the mixture energy and entropy fluxes, as well as stress and couple stress read

$$\mathsf{t}_{ij} = \sum_{\alpha=1}^{N} \left(\mathsf{t}_{ij}^{\alpha} - \varrho^{\alpha} C_i^{\alpha} C_j^{\alpha}\right) , \qquad Q_i = \sum_{\alpha=1}^{N} \left(Q_i^{\alpha} + \varrho^{\alpha} V^{\alpha} C_i^{\alpha}\right) , \tag{3.44}$$

$$\mathsf{M}_{ij} = \sum_{\alpha=1}^{N} \left(\mathsf{M}_{ij}^{\alpha} - \varrho^{\alpha} Z_i^{\alpha} C_j^{\alpha}\right) , \qquad \phi_i = \sum_{\alpha=1}^{N} \left(\phi_i^{\alpha} + \varrho^{\alpha} H^{\alpha} C_i^{\alpha}\right) , \tag{3.45}$$

where C_i^{α} denotes the relative velocity (3.3), while Z_i^{α}, V^{α} and H^{α} are the relative fields of angular momentum, energy and entropy (per unit mass), viz.

$$Z_i^{\alpha} = L_i^{\alpha} - L_i , \qquad V^{\alpha} = E^{\alpha} - E , \qquad H^{\alpha} = \eta^{\alpha} - \eta . \tag{3.46}$$

Additionally, naming the productions and supplies of mass, linear and angular momenta, energy and entropy respectively by Γ, κ_i, g_i, N_i, K_i, P, R, ς and s, and summing (3.25), (3.27), (3.29), (3.31) and (3.33) over all α, one derives from (3.1), (3.2) and (3.43)–(3.46) the relations

$$\Gamma = \frac{1}{\varrho} \sum_{\alpha=1}^{N} \varrho^{\alpha} \Gamma^{\alpha} , \qquad \kappa_i + g_i = \frac{1}{\varrho} \sum_{\alpha=1}^{N} \varrho^{\alpha} \left(\kappa_i^{\alpha} + g_i^{\alpha}\right) , \tag{3.47}$$

$$N_i + K_i = \frac{1}{\varrho} \sum_{\alpha=1}^{N} \varrho^{\alpha} \left(N_i^{\alpha} + K_i^{\alpha}\right) , \qquad P + R = \frac{1}{\varrho} \sum_{\alpha=1}^{N} \varrho^{\alpha} \left(P^{\alpha} + R^{\alpha}\right) , \tag{3.48}$$

$$\varsigma + s = \frac{1}{\varrho} \sum_{\alpha=1}^{N} \varrho^{\alpha} \left(\varsigma^{\alpha} + s^{\alpha}\right) . \tag{3.49}$$

But, the conservation of mass, momenta and energy of the mixture inevitably imply the vanishing of their mixture productions ($\Gamma = N_i = P = 0$), while the second law of thermodynamics enforces $\varsigma \geq 0$. Besides that, *as far as attention is restricted to inertial reference frames* (cf. Chap. 4), external supplies and internal productions should be independent of each other, since they are promoted by uncorrelated causes. From this reasoning, (3.47)–(3.49) can be rewritten as

$$\sum_{\alpha=1}^{N} \varrho^{\alpha} \Gamma^{\alpha} = 0 , \qquad \sum_{\alpha=1}^{N} \varrho^{\alpha} \kappa_i^{\alpha} = 0 , \qquad \sum_{\alpha=1}^{N} \varrho^{\alpha} N_i^{\alpha} = 0 , \qquad \sum_{\alpha=1}^{N} \varrho^{\alpha} P^{\alpha} = 0 , \tag{3.50}$$

$$g_i = \frac{1}{\varrho} \sum_{\alpha=1}^{N} \varrho^{\alpha} g_i^{\alpha} , \qquad K_i = \frac{1}{\varrho} \sum_{\alpha=1}^{N} \varrho^{\alpha} K_i^{\alpha} , \qquad R = \frac{1}{\varrho} \sum_{\alpha=1}^{N} \varrho^{\alpha} R^{\alpha} , \tag{3.51}$$

$$s = \frac{1}{\varrho} \sum_{\alpha=1}^{N} \varrho^{\alpha} s^{\alpha} , \qquad \sum_{\alpha=1}^{N} \varrho^{\alpha} \varsigma^{\alpha} \geq 0 . \tag{3.52}$$

Consequently, collecting the results (3.1), (3.2) and (3.25)–(3.52), there arise the conservation laws of mass, linear and angular momenta and energy, which are identical to those for a single medium[6]

[6] The appropriate equations for single polar media can be derived from (3.25)–(3.34) by simply setting $N = 1$ and $\Gamma^{\alpha} = \kappa_i^{\alpha} = N_i^{\alpha} = P^{\alpha} = 0$.

$$\frac{\partial \varrho}{\partial t} + \frac{\partial}{\partial x_i}(\varrho v_i) = 0 \,, \tag{3.53}$$

$$\frac{\partial \varrho v_i}{\partial t} + \frac{\partial}{\partial x_j}(\varrho v_i v_j - \mathsf{t}_{ij}) = \varrho g_i \,, \tag{3.54}$$

$$\frac{\partial \varrho L_i}{\partial t} + \frac{\partial}{\partial x_j}(\varrho L_i v_j - \mathsf{M}_{ij}) = \varrho K_i \,, \tag{3.55}$$

$$\frac{\partial \varrho E}{\partial t} + \frac{\partial}{\partial x_i}(\varrho E v_i + Q_i) = \varrho R \,, \tag{3.56}$$

together with the identifications

$$L_i = \epsilon_{ijk} x_j v_k + \sigma_i \,, \qquad E = e + \tfrac{1}{2} v_i v_i + \tfrac{1}{2}\sigma_i s_i \,, \tag{3.57}$$

$$\mathsf{M}_{il} = \epsilon_{ijk} x_j \mathsf{t}_{kl} + \mathsf{m}_{il} \,, \qquad Q_j = q_j - \mathsf{t}_{ij} v_i - \mathsf{m}_{ij} s_i \,, \tag{3.58}$$

$$K_i = \epsilon_{ijk} x_j g_k + c_i \,, \qquad R = r + g_i v_i + c_i s_i \,, \tag{3.59}$$

as well as the entropy inequality

$$\frac{\partial \varrho \eta}{\partial t} + \frac{\partial}{\partial x_i}(\varrho \eta v_i + \phi_i) - \varrho s \geq 0 \,. \tag{3.60}$$

It should be observed that (3.35)–(3.52) give also rise to the definitions of spin, its inertia and production, body couple, Voigt couple stress, internal energy and its production, radiation supply and heat flux, viz.

$$\sigma_i = \frac{1}{\varrho}\sum_{\alpha=1}^{N} \varrho^\alpha \sigma_i^\alpha, \qquad \mathsf{I}_{ij} = \frac{1}{\varrho}\sum_{\alpha=1}^{N} \varrho^\alpha \mathsf{I}_{ij}^\alpha, \qquad \sum_{\alpha=1}^{N} \varrho^\alpha \nu_i^\alpha = 0, \tag{3.61}$$

$$c_i = \frac{1}{\varrho}\sum_{\alpha=1}^{N} \varrho^\alpha c_i^\alpha, \qquad \mathsf{m}_{ij} = \sum_{\alpha=1}^{N}\big(\mathsf{m}_{ij}^\alpha - \varrho^\alpha \Sigma_i^\alpha C_j^\alpha\big), \tag{3.62}$$

$$e = \frac{1}{\varrho}\sum_{\alpha=1}^{N} \varrho^\alpha \left(e^\alpha + \frac{C_i^\alpha C_i^\alpha}{2} + \mathsf{I}_{ij}^\alpha \frac{S_i^\alpha S_j^\alpha}{2}\right), \tag{3.63}$$

$$\sum_{\alpha=1}^{N} \varrho^\alpha (\varepsilon^\alpha + \kappa_i^\alpha C_i^\alpha + \nu_i^\alpha S_i^\alpha) = 0 \,, \quad r = \frac{1}{\varrho}\sum_{\alpha=1}^{N} \varrho^\alpha \big(r^\alpha + g_i^\alpha C_i^\alpha + c_i^\alpha S_i^\alpha\big) \,, \tag{3.64}$$

$$q_k = \sum_{\alpha=1}^{N}\Bigg[q_k^\alpha - \mathsf{t}_{ik}^\alpha C_i^\alpha - \mathsf{m}_{ik}^\alpha S_i^\alpha + \varrho^\alpha \left(W^\alpha + \frac{C_i^\alpha C_i^\alpha}{2} + \mathsf{I}_{ij}^\alpha \frac{S_i^\alpha S_j^\alpha}{2}\right) C_k^\alpha - \varrho^\alpha \mathsf{J}_{ij}^\alpha \frac{s_i s_j}{2} C_k^\alpha\Bigg] \,, \tag{3.65}$$

where C_i^α is the relative velocity (3.3), while Σ_i^α, S_i^α, J_{ij}^α and W^α are defined by

$$\Sigma_i^\alpha = \sigma_i^\alpha - \sigma_i \,, \qquad S_i^\alpha = (\mathsf{I}_{ij}^\alpha)^{-1}\sigma_j^\alpha - (\mathsf{I}_{ij})^{-1}\sigma_j \,, \tag{3.66}$$

$$\mathsf{J}_{ij}^\alpha = \mathsf{I}_{ij}^\alpha - \mathsf{I}_{ij} \,, \qquad W^\alpha = e^\alpha - e \,. \tag{3.67}$$

Several remarks are relevant here, since the equations above do not coincide completely with any of the previous continuum theories for mixtures with microstructure cited in this Chapter, viz. [7, 240, 411]. Concerning the theory of Kelly [240], there is in fact no real disagreement at all: the definitions of mixture stress, spin and couple stress, as well as the balance equations of spin presented here are all in concordance with Kelly's results. The only difference is that Kelly has left the kinetic energy of spin and the power fluxes due to couple stresses hidden within the definitions of internal energy and heat flux, respectively, in contrast to the present approach, in which these properties are explicitly accounted for.

On the other hand, the theories of Allen & Kline [7] and Twiss & Eringen [411] exhibit just slight deviations from the results presented here, but of profound conceptual relevance. The key for the understanding of such differences rests upon the definition of the mixture couple stress (3.62). Both Allen & Kline and Twiss & Eringen committed the same mistake by adopting the expression for the mixture stress $(3.44)_1$ as "paragon" to define the appropriate relation for the mixture couple stress[7]. Doing so, they entered in conflict with the fact that couple stresses must be after all equivalent to influxes of spin. Effectively, they proposed that the diffusive contribution to (3.62) should be, in our notation, of the form $\varrho^\alpha I^\alpha_{ik} S^\alpha_k C^\alpha_j$ (instead of $\varrho^\alpha \Sigma^\alpha_i C^\alpha_j$), preserving so the generic structure

"inertia density $\times$ relative velocity $\times$ translational diffusive velocity"

found in $(3.44)_1$. From the discussion presented in Sect. 3.2, and in particular from (3.12), it becomes clear that the right structure for the diffusive fluxes of momenta are actually

"mass density $\times$ specific relative momentum $\times$ translational diffusive velocity".

The fact that, in the particular case of linear momentum, both structures become equivalent, turns therefore to be merely incidental[8].

Finally, it should be noticed that the last term on the right-hand side of (3.65) does not appear in the expression for the mixture heat flux suggested by Allen & Kline [7], since it was introduced ad hoc by the authors into the energy balance equation of the constituents (3.56) as an additional contribution due to a "net production of substructure kinetic energy". Such a bizarre form of the constituent

[7] Actually, Twiss & Eringen [411] did not present an explicit expression for the couple stress but for an akin quantity which they named the "stress moment" t^α_{ijk}, and this in terms of the so called "microinertia" i^α_{ij} and "diffusion gyration" v^α_{ij}. Relations between such quantities and those used here were nevertheless indicated at the end of their work (see also [123]), viz. $\mathsf{m}^\alpha_{ij} = \epsilon_{jml} t^\alpha_{ilm}$, $\mathsf{I}^\alpha_{ij} = i^\alpha_{kk}\delta_{ij} - i^\alpha_{ij}$ and $s^\alpha_i = \frac{1}{2}\epsilon_{ilk} v^\alpha_{kl}$. A similar situation occurred also in the paper of Allen & Kline [7], although they employed different names.

[8] The interpretation of stress and couple stress as influxes of momenta is deeply rooted in the metaphorical sense of continuum (see Sect. 1.2), in contrast to the concept of natural continuum introduced in Def. 1.2.1, which gives rise to the classical notion of stress (a historical exposition of these two contrasting concepts is offered in the treatise by Love [281]). Actually, the view of stress and couple stress as influxes of momenta is most often advantageous and should never be overlooked. As commented by Maxwell [297]:

> "*The fundamental dynamical idea of matter, as capable by its motion of becoming the recipient of momentum and energy, is so interwoven with our forms of thought that, whenever we catch a glimpse of it in any part of nature, we feel that a path is before us leading, sooner or later, to the complete understanding of the subject.*" (pp. 181)

balance equation of energy was later criticized by Twiss & Eringen [411], who chose instead to incorporate it as a source term in an additional balance equation for the inertia tensor of the microstructure. Here, the last term on the right-hand side of (3.65) arises quite naturally from $(3.36)_2$, $(3.44)_2$ and (3.62) as an energy flux due to the coupling of translational diffusion with inertial effects.

4. Frame Invariance in Reacting Mixtures of Liquid Crystals

Es ist ein herrliches Gefühl, die Einheitlichkeit eines Komplexes von Erscheinungen zu erkennen, die der direkten sinnlichen Wahrnehmung als ganz getrennte Dinge erscheinen.

Albert Einstein, [119]

One of the pillars of continuum mechanics and thermodynamics is the assumption that mass, energy and momenta, as well as other additive properties, can change in time by means of three distinct processes (cf. (3.16), (3.19) and (3.23)): local exchanges by fluxes and contact interactions, internal production or dissipation, and volume supplies via long range actions. The latter are sometimes also called external supplies – partly by force of habit, to facilitate their distinction from the terms intuitively related to internal production and dissipation, and partly to express the idea that such supplies are due to extrinsic causes, like gravity, radiation from distant sources and apparent forces provoked by the motion of a non-inertial observer. There are some situations, however, in which such a separation into internal and external sources becomes problematic, if not artificial. A simple example is the production of magnetization in a paramagnetic material, which depends not only on the external and local magnetic fields, but also on the additional magnetic fields arising from all other magnetized points of the medium [57, 126, 127, 134, 217, 225, 339, 341]. In this Chapter a much more dramatic situation is analyzed, recently called *Müller's paradox* [130]: it involves a kind of "apparent production" of spin and internal energy in a mixture of liquid crystals, by means of microstructural inertial effects.

4.1 Anisotropic fluids

Despite the efforts towards a thoroughgoing theory of chemically reacting mixtures of microstructured continua (e.g. [7, 78, 109, 132, 411]), a judicious study of frame invariance and inertial effects in such media has remained terra incognita up to recent times. This situation started to change some months ago, after Müller's [319] analysis of frame invariance in mixtures of polymeric liquid crystals. His approach, however, was based on some critical assumptions, like the reckoning of frame dependent balance equations and the supposition that the constituent productions of director momentum should be objective (i.e., independent of the referential frame) even in the presence of chemical reactions. These conjectures finally led him to the counterintuitive result that the internal energy of such mixtures should be depen-

dent on the observer (frame of reference), a conclusion which will be from now on referred to as *Müller's paradox*[1]. The main objective of this Chapter is to prove that the paradox mentioned above is completely expunged through the careful reckoning of all inertial effects which can occur in such mixtures.

Balance equations for liquid crystals have been introduced in continuum mechanics by Ericksen [120, 121] and Leslie [266, 267, 269, 270], basing on the pioneering work of Oseen and Frank, among others[2] [145, 335]. Owing to this, the continuum theory of liquid crystals is sometimes referred as the "Ericksen–Leslie theory" although its formal name, which has been used by Ericksen [120, 122] and Leslie [264, 265] and goes back (at least) to Oseen [335], is theory of *anisotropic fluids*.

Presently, the modern method of derivation of the balance equations for liquid crystals follows just the same steps as in the case of polar media, reflecting the fact that both materials have a microstructure whose evolution is based on the concept of spin. Indeed, rephrasing the definitions of Chap. 3, one can introduce the spin of a liquid crystal as (cf. (2.5) and (3.37))

$$\sigma_i = \mathsf{I}_{ij} s_j \ , \qquad \text{with} \qquad \mathsf{I}_{ij} = \mathsf{I}_{ji} = d^2 \delta_{ij} - d_i d_j \ , \tag{4.1}$$

where $d_i(x_j, t)$ denotes the *director*, viz. a vector of constant magnitude ($d = \sqrt{d_i d_i}$ = const.) which points towards the direction of molecular alignment that specifies the axis of rotational symmetry of the fluid. Therefore, the fundamental difference between polar and anisotropic fluids is the fact that the latter (in contrast to polar fluids) possesses an anisotropic microstructure whose orientation plays a crucial role in the description of the medium. In other words, the material response depends strongly on the field d_i. Definition $(4.1)_2$ stresses the fact that the liquid crystal particles are *metaphorically* depicted as extremely slender rods, in such a way that the component of spin parallel to the director vanishes (seeing that the spin velocity s_i is bounded) while the spin component perpendicular to d_i is given by

$$\sigma_{i_\perp} = \sigma_i = \epsilon_{ijk} d_j \dot{d}_k = \left(\boldsymbol{d} \times \dot{\boldsymbol{d}} \right)_i \ , \tag{4.2}$$

with $\dot{d}_i$ denoting the material time derivative of the director d_i. This can be generically defined for any arbitrary scalar, vector or tensor valued quantity $\mathsf{Q}(x_i, t)$ as (v_i is as usual the translational velocity)

$$\dot{\mathsf{Q}} = \frac{\partial \mathsf{Q}}{\partial t} + v_k \frac{\partial \mathsf{Q}}{\partial x_k} \ . \tag{4.3}$$

Accordingly, following the same arguments leading to (4.2), one derives the definitions

[1] Actually, Müller had been aware of the troubles with the frame invariance of the internal energy in a liquid crystal mixture during almost thirty years: as early as 1975 Dunwoody [109] has propounded a reticent attempt towards a theory of mixtures of liquid crystals, in which he refers in a footnote to a private communication by Müller stating the conviction of the latter on the frame dependence of the internal energy of such mixtures, as long as chemical reactions are taking place.

[2] The literature on the physics of liquid crystals is extensive and there is a number of interesting review articles and treatises on the subject, e.g. [92, 103, 232, 255, 393].

$$\mathsf{m}_{il} = \epsilon_{ijk} d_j \Pi_{kl} \ , \qquad\qquad c_i = \epsilon_{ijk} d_j k_k \ , \tag{4.4}$$

where Π_{ij} and k_i denote the director fields of stress and body force, respectively.

Once the relation between polar and anisotropic fluids is established, it turns possible to use the results of Chap. 3 to derive the appropriate balance equations of mass, momenta, energy and entropy for a liquid crystal. Effectively, the sought equations are precisely (3.53)–(3.60), which with the aid of (4.2)–(4.4) can be rewritten as

$$\dot{\varrho} + \varrho \frac{\partial v_l}{\partial x_l} = 0 \ , \tag{4.5}$$

$$\varrho \dot{v}_k - \frac{\partial \mathsf{t}_{kl}}{\partial x_l} = \varrho g_i \ , \tag{4.6}$$

$$\varrho \left(\epsilon_{ijk} d_j \dot{d}_k + \epsilon_{ijk} x_j v_k \right)^{\cdot} - \frac{\partial}{\partial x_l} \left(\epsilon_{ijk} d_j \Pi_{kl} + \epsilon_{ijk} x_j \mathsf{t}_{kl} \right) = \varrho \left(\epsilon_{ijk} d_j k_k + \epsilon_{ijk} x_j g_k \right) \ , \tag{4.7}$$

$$\varrho \left(e + \tfrac{1}{2} (\dot{d})^2 + \tfrac{1}{2} v^2 \right)^{\cdot} + \frac{\partial}{\partial x_l} \left(q_l - \Pi_{il} \dot{d}_i - \mathsf{t}_{il} v_i \right) = \varrho \left(k_k \dot{d}_k + g_k v_k \right) \ , \tag{4.8}$$

$$\frac{\partial \varrho \eta}{\partial t} + \frac{\partial}{\partial x_i} \left(\varrho \eta v_i + \phi_i \right) - \varrho s \geq 0 \ . \tag{4.9}$$

It must be emphasized that the systems of balance equations (3.53)–(3.60) and (4.5)–(4.9) are, in principle, equivalent for single component liquid crystals, although the last one is usually preferred in the literature, because it yields the so-called balance equation of director momentum, as will be shown soon. Nevertheless, *for mixtures of liquid crystals only the system* (3.53)–(3.60) *has physical meaning*, since distinct chemical components may be oriented in different directions, frustrating the possibility of defining a "mixture director". This important fact has passed unnoticed during many years, leading authors of early theories of liquid crystal mixtures to erroneous conclusions (see e.g. [109]).

Having reviewed some essentials of the continuum theory of (single component) liquid crystals, this discussion turns now attention towards chemically reacting mixtures of them. In particular, entropy will be no longer considered in this Chapter, which predominantly dwells upon the intricate transformation properties of the balance equations of internal energy and spin, with respect to changes of observer (i.e., of reference frame).

4.2 Liquid crystal mixtures and Müller's paradox

The current Section introduces the paradox of frame dependence of the internal energy in a reacting mixture of liquid crystals, as posed by Müller [319]. This is accomplished by extracting from the *correct* equations – (4.10)–(4.13) below – their abridged versions adopted in [319].

Consider a mixture of N anisotropic fluids, all having the same translational velocity v_i and temperature T, but possessing different mass densities ϱ^α ($\alpha = 1, 2, \ldots, N$) as well as distinct directors d_i^α. The individual constituents are

assumed to be distinguished only by the lengths of their respective directors, viz. $d^\alpha = \sqrt{d_i^\alpha d_i^\alpha} = \text{const}$. For simplicity, body supplies are assumed absent, with the exception of the inertial forces produced by an eventual motion of the reference frame.

As discussed in the last Section, the appropriate balance equations for liquid crystals are just the very same as for polar fluids, reflecting the fact that both materials have a microstructure whose evolution is based on the concept of spin. Hence, for the case of a chemically reacting mixture of liquid crystals, there follows from (3.25)–(3.42) and (4.1)–(4.4) the constituent balance equations of mass, linear momentum, angular momentum and energy

$$\dot{\varrho}^\alpha + \varrho^\alpha \frac{\partial v_l}{\partial x_l} = \varrho^\alpha \Gamma^\alpha \,, \tag{4.10}$$

$$\varrho^\alpha \dot{v}_k - \frac{\partial \mathsf{t}_{kl}^\alpha}{\partial x_l} = \varrho^\alpha \left(\kappa_k^\alpha - \Gamma^\alpha v_k\right) + \underbrace{\varrho^\alpha i_k}_{=0 \text{ in [319]}} \,, \tag{4.11}$$

$$\begin{aligned} &\varrho^\alpha \left(\epsilon_{ijk} d_j^\alpha \dot{d}_k^\alpha + \epsilon_{ijk} x_j v_k\right)^{\cdot} - \frac{\partial}{\partial x_l}\left(\epsilon_{ijk} d_j^\alpha \Pi_{kl}^\alpha + \epsilon_{ijk} x_j \mathsf{t}_{kl}^\alpha\right) \\ &\qquad = \varrho^\alpha \left[N_i^\alpha - \Gamma^\alpha \left(\epsilon_{ijk} d_j^\alpha \dot{d}_k^\alpha + \epsilon_{ijk} x_j v_k\right)\right] + \underbrace{\varrho^\alpha \left(\epsilon_{ijk} d_j^\alpha l_k^\alpha + \epsilon_{ijk} x_j i_k\right)}_{=0 \text{ in [319]}} \,, \end{aligned} \tag{4.12}$$

$$\begin{aligned} &\varrho^\alpha \left[e^\alpha + \tfrac{1}{2}(\dot{d}^\alpha)^2 + \tfrac{1}{2} v^2\right]^{\cdot} + \frac{\partial}{\partial x_l}\left(q_l^\alpha - \Pi_{il}^\alpha \dot{d}_i^\alpha - \mathsf{t}_{il}^\alpha v_i\right) \\ &\qquad = \varrho^\alpha \left\{P^\alpha - \Gamma^\alpha \left[e^\alpha + \tfrac{1}{2}(\dot{d}^\alpha)^2 + \tfrac{1}{2} v^2\right]\right\} + \underbrace{\varrho^\alpha \left(l_k^\alpha \dot{d}_k^\alpha + i_k v_k\right)}_{=0 \text{ in [319]}} \,, \end{aligned} \tag{4.13}$$

where $\varrho^\alpha \Gamma^\alpha$, $\varrho^\alpha \kappa_i^\alpha$, $\varrho^\alpha N_i^\alpha$ and $\varrho^\alpha P^\alpha$ are the constituent production densities of mass, momenta and total energy, while t_{ij}^α, Π_{ij}^α, e^α and q_i^α denote, respectively, the Cauchy stress, the director stress, the specific internal energy and the heat flux density of the constituent α. Further, i_k and l_k^α are inertial (apparent) accelerations, necessary to make the system of balance equations (4.10)–(4.13) valid in arbitrary reference frames (see e.g. [275, 317]). These inertial accelerations are defined, as usual, by the condition that the relative accelerations $(\dot{v}_i - i_i)$ and $(\ddot{d}_i^\alpha - l_i^\alpha)$ are objective vectors, with $i_k = l_k^\alpha = 0$ holding for inertial observers. Since i_k and l_k^α are produced by extrinsic actions (motion of observer) they pertain to the body forces g_k and k_k, in such a manner that in the absence of body supplies generated by external fields, like those of electromagnetic or gravitational origin, there hold the identities $g_k^\alpha = i_k$ and $k_k^\alpha = l_k^\alpha$. Finally, Eq. (4.12) can be simplified with the aid of (4.11) to the balance equation of spin

$$\epsilon_{ijk} d_j^\alpha \left[\varrho^\alpha \ddot{d}_k^\alpha - \frac{\partial \Pi_{kl}^\alpha}{\partial x_l} + \varrho^\alpha \Gamma^\alpha \dot{d}_k^\alpha \right] = \epsilon_{ijk} \mathsf{t}_{kj}^\alpha + \epsilon_{ijk} \Pi_{kl}^\alpha \frac{\partial d_j^\alpha}{\partial x_l} + \varrho^\alpha \left(N_i^\alpha - \epsilon_{ijk} x_j \kappa_k^\alpha \right) + \underbrace{\varrho^\alpha \epsilon_{ijk} d_j^\alpha l_k^\alpha}_{=0 \text{ in } [319]} . \quad (4.14)$$

It must be emphasized that (4.10)–(4.14) are written in fully invariant form, being therefore valid in inertial as well as non-inertial reference frames. In contrast, it is worthy noticing that the effects of inertial accelerations were neglected in [319] by setting $i_k = l_k^\alpha = 0$, consequently rendering the system (4.10)–(4.13) *frame dependent*. The importance of inertial effects will become clearer later on.

Müller's paradox. The first step taken by Müller in [319] was to rewrite (4.14) as a balance equation of director momentum, by identifying the terms between square brackets in that equation with a production density $\varrho^\alpha g_k^\alpha$, viz.

$$\varrho^\alpha \ddot{d}_k^\alpha - \frac{\partial \Pi_{kl}^\alpha}{\partial x_l} = \varrho^\alpha \left(g_k^\alpha - \Gamma^\alpha \dot{d}_k^\alpha \right) \quad (4.15)$$

(recall that l_k^α was neglected in [319]), with the rest of (4.14) giving rise to the compatibility relation

$$\mathsf{t}_{[kj]}^\alpha + \frac{\partial d_{[j}^\alpha}{\partial x_l} \Pi_{k]l}^\alpha - \varrho^\alpha \left(d_{[j}^\alpha g_{k]}^\alpha + \tfrac{1}{2} \epsilon_{ijk} N_i^\alpha - x_{[j} \kappa_{k]}^\alpha \right) = 0 , \quad (4.16)$$

where the indices within square brackets indicate skew-symmetrization, e.g. $\mathsf{t}_{[kj]} = \frac{1}{2}(\mathsf{t}_{kj} - \mathsf{t}_{jk})$.

Further, it was assumed that the sum over all α of the production densities of mass, total momenta and energy should vanish, i.e.

$$\sum_{\alpha=1}^{\nu} \varrho^\alpha \Gamma^\alpha = 0 , \qquad \sum_{\alpha=1}^{\nu} \varrho^\alpha \kappa_i^\alpha = 0 , \qquad \sum_{\alpha=1}^{\nu} \varrho^\alpha N_i^\alpha = 0 , \qquad \sum_{\alpha=1}^{\nu} \varrho^\alpha P^\alpha = 0 , \quad (4.17)$$

and that the mixture fields of mass density, Cauchy stress, internal energy density and heat flux density were given respectively by[3]

$$\varrho = \sum_{\alpha=1}^{\nu} \varrho^\alpha , \qquad \mathsf{t}_{ij} = \sum_{\alpha=1}^{\nu} \mathsf{t}_{ij}^\alpha , \qquad \varrho e = \sum_{\alpha=1}^{\nu} \varrho^\alpha e^\alpha , \qquad q_i = \sum_{\alpha=1}^{\nu} q_i^\alpha . \quad (4.18)$$

Consequently, by subtracting (4.11) and (4.15) from (4.13) (with $i_k = l_k^\alpha = 0$) and further summation of the result over all α, the following balance equation of internal energy for the mixture could be derived:

$$\varrho \dot{e} + \frac{\partial q_l}{\partial x_l} = \left\{ \mathsf{t}_{kl} \frac{\partial v_k}{\partial x_l} + \sum_{\alpha=1}^{\nu} \left(\frac{\partial \dot{d}_k^\alpha}{\partial x_l} \Pi_{kl}^\alpha - \varrho^\alpha \dot{d}_k^\alpha g_k^\alpha \right) \right\} + \sum_{\alpha=1}^{\nu} \tfrac{1}{2} \varrho^\alpha \Gamma^\alpha (\dot{d}^\alpha)^2 . \quad (4.19)$$

[3] The definitions $(4.18)_{3,4}$ – though not wrong – are not the most familiar ones in the modern theory of mixtures [7, 132, 315, 405, 411], see Subsect. 4.6.

In closing, Müller [319] supposed that the production g_k^α should be an objective quantity, implying that the term between curly brackets in (4.19) would be an objective scalar (due to (4.16), $(4.18)_2$, $(B.2)_2$, (B.5) and (B.9)). Hence, assuming that q_i was an objective vector, he finally arrived at the paradoxical conclusion that the internal energy e should be frame dependent – contrary to what would be naturally expected – because the last term on the right hand-side of (4.19) was certainly not objective.

4.3 Comment on Müller's paper, and outline of the solution to the paradox

The arguments presented in [319] are based on our common experience with mixtures of structureless fluids in arbitrary frames of reference. Undoubtedly, a straightforward application of the same concepts to microstructured mixtures is quite compelling – and indeed absolutely right *when referring to inertial frames*. Nevertheless, Müller's paradox is a clear indication that things are not so straightforward in the case of non-inertial frames of reference. Indeed, it is going to be shown here that some fundamental concepts of the classical theory of mixtures must be revised in the case of (micro-)structured media, and that these modifications change markedly the way we understand chemical reactions and constituent interactions.

The necessary modifications mentioned above are explained in detail along the next sections, and their main features can be resumed here beforehand as follows:

- The production density of director momentum g_k^α cannot be an objective quantity when chemical reactions are taking place. This is evident from the invariant reformulation of (4.15), namely the balance equation of director momentum (4.23).
- Inertial forces and couples acting on the mixture do not always coincide with the sum of the inertial forces and couples exerted upon the individual constituents. This is specially marked in the presence of chemical reactions and phase changes, which rapidly modify the rotational inertia of the microstructure, producing as consequence additional inertial effects (see (4.30)–(4.32)).
- Of course, such differences between the inertial effects acting upon the mixture and on the constituents must be compensated somehow. And this is precisely the final step toward the solution of the paradox: in chemically reacting mixtures of microstructured fluids, contrary to what happens in ordinary mixtures, *the sum of the productions of total angular momentum, $\varrho^\alpha N_i^\alpha$, and energy, $\varrho^\alpha P^\alpha$, are generally not objective*! Consequently, whereas such sums evidently vanish with respect to inertial frames – due to the conservation of total energy and angular momentum of the mixture – the supposition that they should also vanish in the case of non-inertial frames of reference cannot be maintained (see Sect. 4.5).
- The non-objective (and generally non-vanishing) parts of the sums of these productions introduce additional inertial effects, which eliminate the already mentioned discrepancy between mixture inertial effects and their sum over all constituents. Therefore, the mixture balance equations remain invariant and there occurs no

violation of the usual requirements of conservation of total momenta and energy of the mixture. These features are indicated in (4.34), (4.35), (4.40) and (4.39).

- From the above arguments, it follows that the internal energy of the mixture (as well as those of the constituents) is an objective scalar, as it should be. No paradox arises.

It is not expected that the reader has become convinced of the solution merely with the few lines written above. But it is hoped that the thoroughgoing analysis discussed in the next sections succeeds in doing this job.

4.4 On the invariance of the constituent balance equations

One of the important achievements of Müller's 1968 paper on (structureless) mixtures [315] was the recognition that the production of linear momentum of the α-th constituent, viz. κ_i^α, should not be an objective vector. Instead, the difference $(\kappa_i^\alpha - \Gamma^\alpha v_i^\alpha)$ must be objective (v_i^α denoting the translational velocity of the constituent α), as can be easily inferred from the frame invariance of (4.11) and the objectivity of the relative acceleration $(\dot{v}_k^\alpha - i_k^\alpha)$. The physical argument presented by him was that the production κ_i^α should consist of two parts: one due to constituent interactions (supposed to be objective) and another one related to the production of mass by the chemical reaction. This last he assumed to have the generic form $\Gamma^\alpha u_i^\alpha$, where u_i^α is the mean velocity of the newly created mass of the α-th constituent. Of course, the relative velocity $(u_i^\alpha - v_i^\alpha)$ is objective (cf. $(\mathrm{B}.2)_1$ and $(\mathrm{B}.7)_1$). Curiously, similar arguments form the basis of the solution to Müller's paradox.

The assumption that the production of director momentum of the α-th constituent, viz. g_k^α, is an objective vector is rather questionable, since it should also describe the constituent production of director momentum by chemical reactions. In order to understand this point better, attention is now focused on the explicit forms of the production densities appearing in (4.10)–(4.13). Inspired by the arguments considered right above, it will be generically assumed here that

all interaction forces are objective,

and further, that

all chemical production densities[4] *can be decomposed in two parts, one due to constituent interactions and another one related to the mass production by chemical reactions.*

With regard to (4.10) and (4.11), this decomposition follows trivially from the reasons presented at the beginning of this section. However, since the effects of translational diffusion are deliberately avoided from this discussion (i.e., $v_i^\alpha = v_i$), one sets for convenience $u_i^\alpha = u_i$, yielding the simplified expression

$$\kappa_i^\alpha = \hat{\kappa}_i^\alpha + \Gamma^\alpha u_i \,, \tag{4.20}$$

[4]The term *chemical production* is adopted here to emphasize that such productions result from constituent interactions and chemical reactions, and do not exist in single media. In the case of spin, a *non*-chemical production term is $\epsilon_{ijk}\mathrm{t}_{kj}^\alpha$ (cf. (4.14)).

where $\hat{\kappa}_i^\alpha$ is the specific interaction force exerted on constituent α by the other chemical species. Consequently, the invariance of (4.10) and (4.11) immediately follows from (4.20) and the objectivity of Γ^α (cf. $(\mathrm{B}.8)_4$).

In a similar way, we can decompose the production density of total angular momentum, viz. $\varrho^\alpha N_i^\alpha$, in four parts, namely spin and moment-of-momentum productions due to interactions and chemical reactions. Hence, denoting by w_i^α the mean director velocity of the newly created mass of the α-th constituent (with $w_i^\alpha d_i^\alpha = 0$, since the director length d^α is constant) and by $\hat{\psi}_i^\alpha$ the specific *director interaction force* exerted on constituent α by the other species, one obtains

$$N_i^\alpha = \epsilon_{ijk} d_j^\alpha \psi_k^\alpha + \epsilon_{ijk} x_j \kappa_k^\alpha \,, \qquad \text{with} \qquad \psi_k^\alpha = \hat{\psi}_k^\alpha + \Gamma^\alpha w_k^\alpha \,, \tag{4.21}$$

where $\varrho^\alpha \psi_k^\alpha$ denotes the *chemical production density of director momentum*.

Finally, using the same arguments for the production of total energy, we derive (cf. (4.13))

$$P^\alpha = \xi^\alpha + \hat{\psi}_k^\alpha \dot{d}_k^\alpha + \tfrac{1}{2}\Gamma^\alpha (w^\alpha)^2 + \hat{\kappa}_k^\alpha v_k + \tfrac{1}{2}\Gamma^\alpha u^2 \,, \tag{4.22}$$

where the objective scalar ξ^α represents the specific *chemical production of internal energy*. Of course, one could also split ξ^α in two parts, one referring to constituent interactions, viz. $\hat{\xi}^\alpha$, and another one related to the mass production by the chemical reaction; this is however unnecessary for the present purposes and therefore, for brevity, only their sum ξ^α is considered here. The second and fourth terms on the right-hand side of (4.22) denote the powers of interaction forces, while the third and fifth terms represent the translational and rotational kinetic energies of the newly created mass by the chemical reaction, with $u_k u_k = u^2$ and $w_k^\alpha w_k^\alpha = (w^\alpha)^2$.

Now, if one inserts (4.21) into (4.14) and designates by $\varrho^\alpha \gamma_k^\alpha$ all terms of that equation involved in the cross product of d_j^α, then the following balance equation of director momentum, and respective compatibility relation, can be obtained (compare with (4.15) and (4.16)):

$$\varrho^\alpha \left(\ddot{d}_k^\alpha - l_k^\alpha \right) - \frac{\partial \Pi_{kl}^\alpha}{\partial x_l} = \varrho^\alpha \left(\gamma_k^\alpha + \psi_k^\alpha - \Gamma^\alpha \dot{d}_k^\alpha \right) \,, \tag{4.23}$$

$$t_{[kj]}^\alpha + \frac{\partial d_{[j}^\alpha}{\partial x_l} \Pi_{k]l}^\alpha - \varrho^\alpha d_{[j}^\alpha \gamma_{k]}^\alpha = 0 \,. \tag{4.24}$$

This invariant form of the balance equation of director momentum is quite instructive. For instance, by comparing (4.23) with (4.15) it can be immediately concluded that, in an inertial frame of reference, where (4.15) is supposed to hold, $g_k^\alpha = \gamma_k^\alpha + \psi_k^\alpha$. In other words, the total production of director momentum was decomposed in two parts: a chemical one (ψ_k^α), which is not objective; and a supplementary objective part (γ_k^α), which persists even in a single medium. In fact, according to (4.21), the chemical production ψ_i^α consists of two contributions, one assigned to constituent interactions and another one related to the production of mass by the chemical reaction, in such a way that the difference $(\psi_k^\alpha - \Gamma^\alpha \dot{d}_k^\alpha)$ is objective. Consequently, since the relative acceleration $(\ddot{d}_k^\alpha - l_k^\alpha)$ is an Euclidean invariant vector by definition, it

follows that the production γ_k^α is objective, a result which is consistent with (4.24) as well as with the theory of single media, for which $\psi_k^\alpha = 0$, $g_k^\alpha = g_k$, $\gamma_k^\alpha = \gamma_k$ and $g_k = \gamma_k$ hold.

In order to derive the balance equation of internal energy, we simply subtract (4.11) and (4.23) from (4.13), obtaining

$$\varrho^\alpha \dot{e}^\alpha + \frac{\partial q_l^\alpha}{\partial x_l} = \left\{ \mathrm{t}_{kl}^\alpha \frac{\partial v_k}{\partial x_l} + \Pi_{kl}^\alpha \frac{\partial \dot{d}_k^\alpha}{\partial x_l} - \varrho^\alpha \gamma_k^\alpha \dot{d}_k^\alpha \right\}$$
$$+ \varrho^\alpha \left\{ P^\alpha - \left(\psi_k^\alpha - \Gamma^\alpha \dot{d}_k^\alpha \right) \dot{d}_k^\alpha - \left(\kappa_k^\alpha - \Gamma^\alpha v_k \right) v_k - \Gamma^\alpha \left[e^\alpha + \tfrac{1}{2} (\dot{d}^\alpha)^2 + \tfrac{1}{2} v^2 \right] \right\}. \quad (4.25)$$

Eq. (4.25) is invariant with respect to Euclidean transformations, provided that e^α and q_i^α are objective. Indeed, the invariance of the terms within curly brackets in the first line of (4.25) can be easily inferred from (4.24), $(\mathrm{B}.2)_2$, (B.5) and (B.9). On the other hand, the second line of the above equation can be rewritten with the aid of (4.22) as

$$\left\{ \xi^\alpha - \Gamma^\alpha e^\alpha + \tfrac{1}{2} \Gamma^\alpha \left(w_k^\alpha - \dot{d}_k^\alpha \right) \left(w_k^\alpha - \dot{d}_k^\alpha \right) + \tfrac{1}{2} \Gamma^\alpha \left(u_k - v_k \right) \left(u_k - v_k \right) \right\}, \quad (4.26)$$

which is obviously an objective scalar (cf. $(\mathrm{B}.2)_1$, $(\mathrm{B}.5)_1$, (B.7) and $(\mathrm{B}.8)_4$).

The analysis carried up to here has shown that no paradox arises on the constituent level. There remains to evaluate what happens during the transition from constituent to mixture equations.

4.5 The solution

A brief inspection of the balance equation of spin (4.14) reveals that the paradox pointed out in [319] is in fact just the tip of the iceberg: when assumptions similar to those used to arrive at (4.19) are applied to (4.14), the results raised are severely self-contradictory. And in this case, the suggestion that the internal energy of the mixture should not be objective simply does not help. It is shown in this section that the answer to this more fundamental contradiction automatically expunges Müller's paradox.

When dealing with liquid crystalline media, most physicists and engineers prefer to describe microstructural evolution through the traditional director velocity field $\dot{d}_i^\alpha$, instead of using the more fundamental field of spin[5] $\sigma_i^\alpha = \epsilon_{ijk} d_j^\alpha \dot{d}_k^\alpha$. For mixtures of liquid crystals, this choice (of a director velocity) can sometimes represent a disadvantage, for no definite director field can be assigned to the mixture. In other words, there is no counterpart of (4.23) for the mixture, whereas a balance equation of mixture spin naturally exists. To derive it, one defines first the sums (cf. e.g. [132]; recall that $v_i^\alpha = v_i$ in the present case)

[5] By "more fundamental" it is meant that the spin is well-defined even when details about molecular shape and stiffness are unknown (see a deeper discussion in [88]). Further, it should be clear that (4.15), (4.16), (4.23) and (4.24) are all derived from the balance equation of spin (4.14).

$$\varrho\sigma_i = \sum_{\alpha=1}^{N} \varrho^\alpha \sigma_i^\alpha \ , \qquad \mathsf{m}_{il} = \sum_{\alpha=1}^{N} \epsilon_{ijk} d_j^\alpha \Pi_{kl}^\alpha \ , \tag{4.27}$$

$$\varrho \mathsf{I}_{ij} = \sum_{\alpha=1}^{N} \varrho^\alpha \mathsf{I}_{ij}^\alpha \ , \quad \text{with} \quad \mathsf{I}_{ij}^\alpha = (d^\alpha)^2 \delta_{ij} - d_i^\alpha d_j^\alpha \ , \tag{4.28}$$

which introduce the mixture fields of specific spin σ_i and couple stress m_{il}. Besides that, I_{ij} and I_{ij}^α represent the specific inertia tensors of the mixture and of the individual liquid crystalline constituents, respectively, with δ_{ij} denoting the Kronecker delta. Hence, after summing (4.14) over all α and using (4.10), $(4.18)_{1,2}$, (4.20), (4.21) and (4.27), the following balance equation of spin for the mixture is obtained:

$$\varrho\dot{\sigma}_i - \frac{\partial \mathsf{m}_{ik}}{\partial x_k} - \epsilon_{ijk}\mathsf{t}_{kj} = \sum_{\alpha=1}^{N} \varrho^\alpha \epsilon_{ijk} d_j^\alpha \left(\psi_k^\alpha + l_k^\alpha\right) \ . \tag{4.29}$$

Now, two situations may be considered:

1. *the reference frame is inertial.* In this case the director inertial acceleration l_k^α is zero by definition, and consequently, due to the conservation of total momenta, the remaining sum on the right-hand side of (4.29) vanishes. What remains is the standard balance equation of spin for a polar medium (see e.g. [82, 133, 268]), with the right-hand side of (4.29) equal to zero.
2. *the reference frame is not inertial.* In the spirit of Sect. 4.2 and [319], one would be tempted to suppose that the first sum on the right-hand side of (4.29) still should vanish, and that the second sum in that equation could be identified with the inertial couple acting on the mixture. But this is false. By definition, the specific inertial couple c_i acting on the mixture is given by the difference between the fields of spin rate observed in a non-inertial reference frame and in an inertial one, viz. (see Appendix B, and in particular (B.14))

$$\begin{aligned} c_i &= \dot{\sigma}_i - \mathsf{O}_{ij} \left(\dot{\sigma}_j\right)_{\text{IO}} \\ &= \tfrac{1}{2} \left\{ \mathsf{I}_{ij}\epsilon_{jpq}\dot{\Omega}_{qp} - \Omega_{ik}\mathsf{I}_{kj}\epsilon_{jpq}\Omega_{qp} + 2\left(\Omega_{ik}\sigma_k + \tfrac{1}{2}\dot{\mathsf{I}}_{ij}\epsilon_{jpq}\Omega_{qp}\right)\right\} \ , \end{aligned} \tag{4.30}$$

where "IO" stands for "inertial observer". The tensor $\mathsf{O}_{ij}(t)$ represents a proper orthogonal transformation, while $\Omega_{ij} = \dot{\mathsf{O}}_{ik}\mathsf{O}_{jk}$ is the (skew-symmetric) tensor of relative angular velocity of the two frames (see Appendix B). It must be emphasized that, in the relation above and in those to follow, all fields are defined for *arbitrary observers* (i.e., *inertial and non-inertial* ones) – except those quantities identified by $(\cdot)_{\text{IO}}$, of course. Clearly, the three terms on the right-hand side of (4.30) correspond respectively to Euler, centrifugal and Coriolis effects. Additionally, it is worthy of noticing the last term of (4.30), which indicates that Coriolis effects can be also produced by changes in the rotational inertia of the mixture. On the other hand, the director inertial acceleration l_k^α can be likewise computed using a similar definition, viz. (cf. (B.6))

$$l_i^\alpha = \ddot{d}_i^\alpha - \mathsf{O}_{ij}\left(\ddot{d}_j^\alpha\right)_{\text{IO}} = \ \dot{\Omega}_{ij} d_j^\alpha - \Omega_{ik}\Omega_{kj} d_j^\alpha + 2\Omega_{ij}\dot{d}_j^\alpha \ , \tag{4.31}$$

from which the Euler, centrifugal and Coriolis accelerations in customary form are readily recognized. Finally, the last sum on the right-hand side of (4.29) can be determined from (4.27), (4.30) and (4.31), yielding (after a somewhat lengthy calculation shown in Appendix C)

$$\sum_{\alpha=1}^{N} \varrho^{\alpha} \epsilon_{ijk} d_j^{\alpha} l_k^{\alpha} = \varrho c_i - \tfrac{1}{2} \epsilon_{jpq} \Omega_{qp} \sum_{\alpha=1}^{N} \varrho^{\alpha} \mathit{\Gamma}^{\alpha} \mathsf{I}_{ij}^{\alpha} \,, \tag{4.32}$$

where use was made of the essential identity

$$\varrho \dot{\mathsf{I}}_{ij} - \sum_{\alpha=1}^{N} \varrho^{\alpha} \dot{\mathsf{I}}_{ij}^{\alpha} = \sum_{\alpha=1}^{N} \varrho^{\alpha} \mathit{\Gamma}^{\alpha} \mathsf{I}_{ij}^{\alpha} \,, \tag{4.33}$$

which is deduced by the combination of (4.10) with $(4.28)_1$. The physical significance of (4.33) must be strongly emphasized: with the help of $(4.28)_1$ one recognizes from (4.33) that changes in the rotational inertia of the mixture can occur not only due to director motion, but also due to interactions between constituents via chemical reactions. Since such a "reactive production" of inertia involves collective constituent interactions, it cannot be captured by the simple sum on the left-hand side of (4.32) and this lack is expressed by the *missing Coriolis effect* which emerges on the right-hand side of that equation. Hence, the inertial couples acting on the mixture do not coincide with the sum of the inertial couples exerted upon the individual constituents. The need for a Coriolis-type effect produced by chemical interactions immediately turns our attention to the objectivity of chemical productions, and from (4.29) one has a unique suspect. The sum over all α of the chemical production of spin is indeed not objective and yields (see (C.3))

$$\sum_{\alpha=1}^{N} \varrho^{\alpha} \epsilon_{ijk} d_j^{\alpha} \psi_k^{\alpha} = \mathsf{O}_{ij} \underbrace{\sum_{\alpha=1}^{N} \left(\varrho^{\alpha} \epsilon_{jpq} d_p^{\alpha} \psi_q^{\alpha} \right)_{\mathrm{IO}}}_{=0} + \tfrac{1}{2} \epsilon_{jpq} \Omega_{qp} \sum_{\alpha=1}^{N} \varrho^{\alpha} \mathit{\Gamma}^{\alpha} \mathsf{I}_{ij}^{\alpha} \,. \tag{4.34}$$

The objective part of (4.34) is zero because it was already inferred from Situation 1. On the other hand, there is no reason to suppose that the non-objective part of (4.34) should vanish for a non-inertial frame, and this is precisely the missing Coriolis effect which one has been looking for!

The results of the two situations analyzed above are truly enlightening. Generically, they state that production terms can be also sources of inertial effects in the mixture. Consequently, *the putative vanishing of the productions of total energy and angular momentum with respect to* any *arbitrary observer is usually not realistic.* For instance, in the case of the mixture of liquid crystals considered here (with $v_i^{\alpha} = v_i$), one finds from (4.32) and (4.34) that the conservation of total angular momentum of the mixture is correctly and most generally expressed by (compare with $(4.17)_3$)

$$\sum_{\alpha=1}^{N} \varrho^{\alpha} \left(N_i^{\alpha} + \epsilon_{ijk} d_j^{\alpha} l_k^{\alpha} \right) = \sum_{\alpha=1}^{N} \varrho^{\alpha} \epsilon_{ijk} d_j^{\alpha} \left(\psi_k^{\alpha} + l_k^{\alpha} \right) = \varrho c_i \,, \tag{4.35}$$

while the more ordinary requirements

$$\sum_{\alpha=1}^{N} \varrho^{\alpha} \epsilon_{ijk} d_j^{\alpha} l_k^{\alpha} = \varrho c_i \qquad \text{and} \qquad \sum_{\alpha=1}^{N} \varrho^{\alpha} N_i^{\alpha} = 0 \tag{4.36}$$

are only valid when chemical reactions are absent or the frame of reference is not rotating.

To the knowledge of this author, this is the first time that an *internal production of inertial effects* is predicted for microstructured mixtures.

With the experience accumulated up to now, it becomes easy to overcome the difficulties met in [319]. First, by summing the constituent balance equations of internal energy (4.25) over all α, one derives with the aid of (4.18) the mixture balance equation

$$\begin{aligned} \varrho \dot{e} + \frac{\partial q_l}{\partial x_l} = & \left\{ \mathsf{t}_{kl} \frac{\partial v_k}{\partial x_l} + \sum_{\alpha=1}^{N} \left(\frac{\partial \dot{d}_k^{\alpha}}{\partial x_l} \Pi_{kl}^{\alpha} - \varrho^{\alpha} \dot{d}_k^{\alpha} \gamma_k^{\alpha} \right) \right\} \\ & + \sum_{\alpha=1}^{N} \varrho^{\alpha} \left\{ P^{\alpha} - \left[\left(\psi_k^{\alpha} - \Gamma^{\alpha} \dot{d}_k^{\alpha} \right) \dot{d}_k^{\alpha} + \tfrac{1}{2} \Gamma^{\alpha} (\dot{d}^{\alpha})^2 \right] \right\} . \end{aligned} \tag{4.37}$$

This equation can be readily compared with its counterpart proposed in [319], viz. (4.19). The first line of (4.37) is quite similar to the first three terms of (4.19). In fact, it can be likewise proved – but now with the help of (4.24) instead of (4.16) – that the term between curly brackets in the first line of (4.37) is indeed objective (cf. $(4.18)_2$, $(B.2)_2$, (B.5) and (B.9)). In contrast, the critical problem raised in [319] concerning the non-objectivity of the last sum in (4.19) does not threaten the balance equation (4.37): from the results discussed in Sect. 4.4 it can be straightforwardly inferred that the second line of (4.37) is actually frame invariant. Effectively, recalling the same arguments used to derive (4.26), the last line of (4.37) can be rewritten with the aid of (4.22) as

$$\sum_{\alpha=1}^{N} \varrho^{\alpha} \left\{ \xi^{\alpha} + \tfrac{1}{2} \Gamma^{\alpha} \left(w_k^{\alpha} - \dot{d}_k^{\alpha} \right) \left(w_k^{\alpha} - \dot{d}_k^{\alpha} \right) \right\} , \tag{4.38}$$

which is evidently an Euclidean-invariant scalar, since ϱ^{α}, ξ^{α}, Γ^{α} and $(w_k^{\alpha} - \dot{d}_k^{\alpha})$ are all objective quantities.

Finally, the sum over all α of the production density of total energy is presented here for completeness. It reads (compare with $(4.17)_4$)

$$\sum_{\alpha=1}^{N} \varrho^{\alpha} P^{\alpha} = \underbrace{\sum_{\alpha=1}^{N} \left(\varrho^{\alpha} P^{\alpha} \right)_{\text{IO}}}_{=0} + \tfrac{1}{8} \epsilon_{ipq} \Omega_{qp} \epsilon_{jkl} \Omega_{lk} \sum_{\alpha=1}^{\nu} \varrho^{\alpha} \Gamma^{\alpha} \mathsf{I}_{ij}^{\alpha} . \tag{4.39}$$

The proof of (4.39) is given through a tedious calculation in Appendix C, which can be likewise used to derive the relation

$$\sum_{\alpha=1}^{N} \varrho^{\alpha} \left[\left(\psi_k^{\alpha} - \Gamma^{\alpha} \dot{d}_k^{\alpha} \right) \dot{d}_k^{\alpha} + \tfrac{1}{2} \Gamma^{\alpha} (\dot{d}^{\alpha})^2 \right]$$

$$= \sum_{\alpha=1}^{N} \left\{ \varrho^{\alpha} \left[\left(\psi_k^{\alpha} - \Gamma^{\alpha} \dot{d}_k^{\alpha} \right) \dot{d}_k^{\alpha} + \tfrac{1}{2} \Gamma^{\alpha} (\dot{d}^{\alpha})^2 \right] \right\}_{\mathrm{IO}} + \tfrac{1}{8} \epsilon_{ipq} \Omega_{qp} \epsilon_{jkl} \Omega_{lk} \sum_{\alpha=1}^{N} \varrho^{\alpha} \Gamma^{\alpha} \mathsf{I}_{ij}^{\alpha} \,. \quad (4.40)$$

Invoking the same arguments presented in Situation 1 of Sect. 4.5, the conservation of total energy of the mixture requires that the sum of $\varrho^{\alpha} P^{\alpha}$ over all α must be zero in an inertial reference frame. But the non-objective part of (4.39) does not need to vanish in all referential frames. Rather, it combines with (4.40) to render the balance equation of internal energy (4.37) frame invariant.

Hence, provided that the heat flux is a frame-invariant vector, the internal energy of the mixture is objective. No paradox emerges.

4.6 Final remarks

The heart of this chapter lies in the cognizance that mixtures of liquid crystals – as well as of other structured fluids – are generally subjected to additional inertial effects produced within the material, as a result of chemical reactions (or phase changes) and the extra degrees of freedom posed by the microstructure. These *internal inertial effects* are mathematical consequences of the non-objectivity of the productions of spin and energy of the mixture, as exemplified by (4.34) and (4.39), and compensate the imbalance between the inertial effects acting on the mixture and the sum of those exerted upon the individual constituents. Since all these additional phenomena are only illusory, i.e. apparent to non-inertial observers, there is no violation of the fundamental axioms of conservation of total energy and angular momentum.

Before closing, it is proper to highlight the generality of the results derived above by adducing some supplementary remarks.

Why do these phenomena not occur in ordinary mixtures?

One could answer this question through a modest pun: a remarkable peculiarity of *ordinary* chemically reacting mixtures is precisely the *extraordinary* simplicity of their production terms.

Effectively, according to the classical theory of mixtures [315, 405], the constituent productions of total momenta and energy are in fact *not* objective (cf. also the short discussion at the beginning of Sect. 4.4). Nevertheless, it can be easily shown that the summation of these productions over all α luckily annihilates every non-objective part of them, rendering *their sum* objective. In other words, a short calculation demonstrates that, for chemically reacting mixtures of structureless fluids, there hold the relations

$$\sum_{\alpha=1}^{N} \varrho^{\alpha}\kappa_{j}^{\alpha} \;=\; \mathsf{O}_{ij} \underbrace{\sum_{\alpha=1}^{N} \left(\varrho^{\alpha}\kappa_{j}^{\alpha}\right)_{\text{IO}}}_{=0} , \qquad \sum_{\alpha=1}^{N} \varrho^{\alpha} N_{i}^{\alpha} \;=\; \mathsf{O}_{ij}\epsilon_{jkl}x_{k} \underbrace{\sum_{\alpha=1}^{\nu} \left(\varrho^{\alpha}\kappa_{l}^{\alpha}\right)_{\text{IO}}}_{=0} , \tag{4.41}$$

$$\sum_{\alpha=1}^{N} \varrho^{\alpha} P^{\alpha} \;=\; \underbrace{\sum_{\alpha=1}^{N} \left(\varrho^{\alpha} P^{\alpha}\right)_{\text{IO}}}_{=0} . \tag{4.42}$$

Therefore, from the conservation of total momenta and energy follows the customary result that the sum over all α of such productions must vanish in an inertial reference frame, and finally, due to the objectivity of their respective sums, such a conclusion can be automatically extended to non-inertial frames as well.

It must be emphasized that this "extraordinary simplicity" found in mixtures of structureless fluids represents in fact *the exception and not the rule*: whenever the rotational inertia of the mixture is not identical to the rotational inertia of the constituents, such an "overall annihilation" of non-objective terms does not apply (cf. (4.33)) and internal inertial effects similar to those appearing in (4.34) and (4.39) are produced.

And what about the rotational part of the internal energy?

A reader used to the literature on the classical theory of diffusion could eventually feel himself somewhat discomfortable with $(4.18)_{3,4}$, since these relations do not introduce any rotational feature in the definitions of internal energy and heat flux of the mixture. Indeed, according to the terminology used by Truesdell [405], the internal energy and heat flux so defined represent in fact the so-called *interior quantities*. It is nevertheless a trivial task to reformulate $(4.18)_{3,4}$ in such a way that e and q_i possess also rotational parts. From physical grounds (and the support of former works on the continuum, statistical and kinetic theories of structured media [7, 46, 84, 85, 132, 149, 156, 171, 411]) it is known that the definitions which fully account for interior and rotational contributions to the internal energy and heat flux of the mixture read (taking for granted the assumption $v_i^{\alpha} = v_i$)

$$\varrho e = \sum_{\alpha=1}^{N} \varrho^{\alpha} e^{\alpha} + \tfrac{1}{2} \sum_{\alpha=1}^{N} \varrho^{\alpha} \mathsf{I}_{ij}^{\alpha} S_{i}^{\alpha} S_{j}^{\alpha} , \qquad q_i = \sum_{\alpha=1}^{N} q_{i}^{\alpha} - \sum_{\alpha=1}^{N} \epsilon_{ijk} d_{j}^{\alpha} \Pi_{kl}^{\alpha} S_{i}^{\alpha} , \tag{4.43}$$

where

$$S_{i}^{\alpha} = \frac{1}{(d^{\alpha})^{2}} \left(\epsilon_{ijk} d_{j}^{\alpha} \dot{d}_{k}^{\alpha} - \mathsf{I}_{ij}^{\alpha} s_j \right) , \qquad \text{with} \qquad s_i = \mathsf{I}_{ij}^{-1} \sigma_j ,$$

denotes the *spin velocity of the constituent α relative to the mixture*. Hence, (4.43) states that the kinetic energy and the mechanical power of the *diffusive spin motion* contribute, respectively, to the internal energy and the heat flux of the mixture, in addition to the interior quantities.

Choosing between definitions $(4.18)_{3,4}$ and (4.43) is basically a matter of taste: the first ones make some calculations easier, whereas the second ones yield more

familiar forms of the balance equations of total and internal energy, involving fewer constituent fields. In fact, by repeating exactly the same procedure presented in Sect. 4.2 – but this time replacing $(4.18)_{3,4}$ by (4.43) – one can infer that the definition of an internal energy with rotational part does not aid to solve Müller's paradox. Finally, even if one refuses both $(4.18)_{3,4}$ and (4.43) in favor of any bizarre definition of internal energy, this does not change the fact that, formally, the Coriolis-like effects occurring in (4.32), (4.34) and (4.39) cannot be simply ignored.

Is the metaphor of rigid rod helpful in the study of chemical reactions?

In an attempt to interpret physically the hypothetical lack of objectivity of the internal energy in chemically reacting mixtures of polymeric liquid crystals, a so-called "cartoon of the chemical reaction" was discussed in [319]. Roughly, it consisted of a single rotating rodlike molecule – a rigid rod – which suddenly disintegrates itself into its elementary atoms (Fig. 4.1).

It seems rather questionable if such an extremely simplistic picture of a chemical reaction can indeed aid to clarify something about the character and the transformation properties of the internal energy in a continuum theory. In particular, It is not evident from [319] why the existence of a non-objective internal energy containing a rotational part would be implied by the fact that internal energy has emerged from the chemical reaction at the expense of the rotational energy of the rod: the description of a conversion of kinetic into internal energy by chemical reactions is in principle the role of the energy balance equation (4.37) and not of some particular definition of internal energy.

Further, it must be understood that "the rod" is just a *metaphor* for a slender, stiff molecule. In reality, the chemical decomposition of such a molecule is of course not instantaneous. In contrast, the metaphor of a rod which breaks into many pieces suggests a sudden process. It seems that both interpretations are mixed in [319], specially in the sentence "*Surely that newly created internal energy must retain the rotational character at least for a while after the decomposition of the rod.*" In the situation under study, the internal energy can only retain a rotational character if the considered atoms are in fact not completely independent; otherwise they would constitute a system of freely translating particles, whose internal energy has no rotational attributes at all. Yet, if these atoms are still weakly connected, then the molecule is not completely decomposed, but rather *in the process of decomposition.* This reasoning is also supported by [319] in a later affirmation: *"when rotational energy turns into internal energy or into heat, there must be a transitional period".* This is certainly correct. Indeed, in the course of this transitional period, the molecules involved in the chemical reaction have formed the so-called *activated* (or *reacting*) *complex* (see e.g. [16, 144]) and they are so distorted during this stage that they cannot be identified with any of the constituents originally present in the mixture (in the current example: neither with the rod, nor with the atoms). However, to describe this situation properly, one must take into account the internal energies of the rodlike molecule and of the activated complex, in contradiction with the assumption [319] that the rod possesses no internal energy. Moreover, the study of

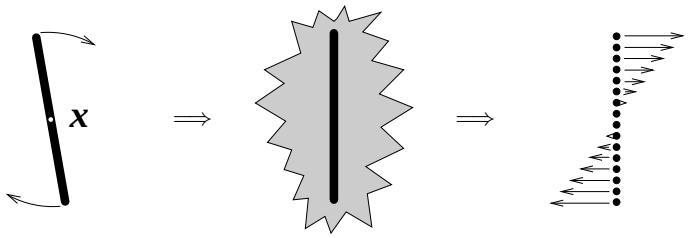


Fig. 4.1. The cartoon of a chemical reaction, according to Müller [319]. Prior to the reaction (*left*), there exists simply the rod, rotating about its center of mass $\boldsymbol{x}$ and possessing no internal energy. Then, when the reaction occurs (*center*), the rodlike molecule is immediately replaced by its atoms (*right*): there is no rod anymore and its rotational energy was completely converted into internal energy[7]

such transitional period is the field of molecular reaction kinetics, which is far away from the scope of our continuum theory of structured mixtures.

Fortunately, the mean life-time of the activated complex is generally negligibly small in comparison to standard time scales of the theory of continuum, implying that the transitional period already mentioned must not be considered. Nevertheless, this means also that the discussion of chemical reactions in a continuum by regarding just a single decomposing molecule is somewhat problematic, since the whole process is expected to elapse too fast: the chemical reaction becomes a singular event and all chemical productions turn to be non-zero only at that unique temporal singularity. So, we have reached the conclusion that the analogy between the proposed cartoon of a disintegrating rod and a chemically reacting mixture of structured continua is not straightforward, because the immediate decomposition of a single molecule cannot reproduce the continuously sustained process of a chemical reaction in the continuum, which involves a huge number of interacting molecules successively reacting within a single material particle.

[7]To be clearer, the system of atoms possesses no translational energy, since its center of mass remains at rest, but there exists an "internal" energy, which is expressed as the sum of the translational diffusive kinetic energies of the individual atoms with respect to the center of mass of the system – i.e., this is the translational analogue to the last term of $(4.43)_1$, cf. e.g. [405].

Part II

Mixtures with Continuous Diversity: General Theory and Applications

Complicating the Simple or Simplifying the Complex?

5. Fundamentals on Continuous Diversity

Dear Tait

$$\nabla = i\frac{\mathrm{d}}{\mathrm{d}x} + j\frac{\mathrm{d}}{\mathrm{d}y} + k\frac{\mathrm{d}}{\mathrm{d}z}$$

What do you call this? Atled?

James Clerk Maxwell[1], [298]

Presently, it seems rather natural to regard any common chemical mixture as composed of a discrete number of chemically distinct species. Some hundred years ago, however, this fact was far from trivial even for the most prominent alchemists, and particularly doubtful for those who did not believe in the atomistic nature of the matter, as exposed by Lucretius [283] more than two thousand years ago. Indeed, since then there was an arduous way to explain, formally, why every substance should present particular physical and chemical properties (see e.g. [13]). Of course, the modern theory of mixtures [7, 32, 50–52, 106, 109, 110, 115, 124, 130, 177, 178, 189, 223, 240, 310, 315–317, 326, 352, 356, 370, 394, 405, 407, 409, 411, 433] was mostly developed under this scheme, with the identification of the constituents being usually performed through a discrete set of labels or indices. Nevertheless, it must be observed that the fundamentals of this theory are in fact based on a much wider realm than that of usual chemical mixtures. This enabled scientists to apply such concepts to many other multicomponent environments, from granular media [32, 106, 326, 394, 407, 433] and bubbly liquids [32] to composite materials [32, 352] and (after a suitable change of terminology) also population dynamics [318, 320, 322, 333, 410]. Ironically, in some of the examples above, the discrete identification of species seems to be a simplified picture of the macroscopic reality. It is basically about such less conventional applications of the mixtures theory that this work will be from now on concerned.

5.1 Raison d'être

An apology is needed to the language employed in this Chapter. In order to exploit the generality of the theme, words like *mixture*, *species*, *constituents* and *diversity* will be often utilized in their broadest sense, instead restricted to their specific

[1] Hamilton's differential operator – written as an inverted delta – was up to that date called "characteristic of operation" [196, 397]. Just some days after Maxwell's letter to Peter G. Tait, the operator's name was definitively changed to *nabla*. On the other hand, the terms *convergence* and *curl* of a vector have been originally proposed by Maxwell to Tait in that same letter [298].

meanings in chemistry, physics or biology. In particular, the neologism *mixture with continuous diversity* is now introduced [129], in order to generically refer to a multicomponent medium made up of a continuous set of mutually interacting components (i.e., constituents whose distinctive properties vary smoothly from one to another).

To illustrate this concept, consider the example of a dry granular medium composed of (roughly) spherical solid particles of the same material but with different sizes. Experience shows that the mechanical response of this medium is strongly dependent on the grain size distribution [172, 173, 222, 224], in such a way that one can expect distinct material behavior, depending on the dimensions of the grains. In other words, the granular medium can be viewed as a mixture of solid particles, of which the different species are classified according to their grain sizes (e.g. diameters). While the gross features of such a medium can be qualitatively understood with the usual mixture theory, by using some discrete classification of the granular species (for example, a two-component mixture of large and small grains, as considered by Savage & Lun [372]), a general theory should take into account the whole grain size distribution, in order to afford *quantitative* predictions. This is particularly true if one intends to describe, quantitatively, complex size effects like grain size segregation [29, 111, 172, 206, 224], or the (more or less) gradual degradation of large grains to smaller ones by erosional phenomena like abrasion and fragmentation [242–244]. However, a modern thermodynamic theory, founded on an appropriate entropy principle capable of dealing with the whole continuous spectrum of grain diameters, is lacking.

Actually, it is not difficult to construct an heuristic procedure to extend the fundamental concepts of some well-known discrete description, in order to obtain a continuous version of it. In fact, such an idea was already used at the end of the 19th century by Volterra [418] (see also the note by Whittaker [428]) to construct a mathematical theory for what he named "functions depending on other functions", nowadays simply called *functionals*, due to Hadamard [193, 194]. More closely related to the framework of multicomponent media, Prager [354] remarked that the translational diffusion phenomenon in an isotropic suspension of rodlike solid particles resembles well diffusive processes in a mixture of species with different diffusion coefficients. On the other hand, the similarity between a gas of non-spherical molecules and what is called here a mixture with continuous diversity was evidenced by Curtiss [84]. Later, Condiff & Brenner [78] took advantage of this analogy to construct a phenomenological theory of fluids composed of orientable particles, using some classical results of the irreversible thermodynamic theory of mixtures.

It is interesting to notice the odd fate associated to the notion of a mixture comprising a continuous variety of constituents: within the frames of the theory of chemical reactions, such an abstraction has its roots in the work of de Donder [104], who outlined it in the first half of 20th century. It seems, however, that the repercussion of de Donder's ideas was not very great at that time, since these fell soon into almost complete oblivion. It took more than thirty years until Aris & Gavalas [11] independently developed a similar concept within exactly the same context – chemical

reaction kinetics. The Aris–Gavalas theory of continuous reactions went far beyond de Donder's and reached the technical and scientific communities on an occasion when polymerization and cracking reactions were urging more effective theoretical descriptions. It has established itself as a prolific mean of modeling extremely complex chemical reactions involving a very large number of constituents in mixtures of which no precise analysis is possible (ex. petroleum processing) [332, 345]. In this sense, it represents a continuum"simplification" of a discrete reality, for it amalgamates reactants into a single lump, in an intuitive process which resembles well the homogenization procedures discussed in Chaps. 1 and 2.

In spite of these merits, scientists outside the proper specialists' circles have been unaware of the kind of mixtures involved on the theory of continuous reactions, a fact which can be justified not only by the rather specialized applications of the theory, but also because of an unfortunate name: such mixtures have been called *continuous mixtures* by chemists, which is just the same name often used to refer to ordinary mixtures of continua (see e.g. [291]). Curiously, once again, after more than thirty years of the publication of the work of Aris & Gavalas [11], another theory for mixtures comprising a continuous variety of constituents has been independently proposed [129]: the theory of mixtures with continuous diversity. Nevertheless, the context in which this last theory has been introduced, as well as its scope, differs conspicuously from the earlier ones. Indeed, the concept of continuous diversity as suggested in [129] is sufficiently general to surpass by far the limits of chemical reactions, and it is in fact not restricted to chemical systems at all, being useful also to the modelling of many different heterogeneous thermodynamic systems, from iceberg ensembles to liquid crystals [46, 77, 78, 132, 135, 166, 432], by modeling them as mixtures of orientations, or sizes, or even abstract characters. Evidently, in most of these situations the continuous diversity hypothesis is not a "simplification" of the reality (like in the theory of continuous reactions) but rather an exact description of it. In any case, the Aris–Gavalas theory constitutes of course a "chemical" particularization of the theory of mixtures with continuous diversity – allowing so possible extensions to less orthodox types of mixtures of the powerful concepts and techniques developed within the frames of continuous reactions during the last decades.

5.2 Mixtures with continuous diversity

Originally, the continuum theory of mixtures (see Chaps. 3 and 4) has been conceived to deal only with a very reduced set of markedly distinct chemical constituents. In other words, in the original theory there are no limits at all in the amount of distinguishing properties between any two chemical components, but the total number of constituents in the mixture is severely restricted to a countable finite set, due to practical reasons. In contrast, there are innumerous situations in nature where exactly the opposite situation is found: mixtures whose species exist in an infinitely large number (non countable), but which are distinguished by just one, two, or a very few particular properties (e.g. size, orientation, age, smoothness).

Continua like the last type of mixture described above have been recently called [129, 132] *mixtures with continuous diversity*. Indeed, natural polydisperse granular media (in which the unique distinguishing feature is the grain size) and fiber suspensions (where fibers are distinguished only by their orientation) are two classical examples of such continua. As discussed in Sect. 5.1, a mixture with continuous diversity can be succinctly regarded as a multicomponent medium made up of a continuous set of mutually interacting components, or in other words, a continuum composed of an infinite number of constituents, whose distinctive properties vary *smoothly* from one to another. Mathematically, such a generalization of classical mixture theory can be readily understood by reckoning, for instance, the constituent field of mass density in an ordinary chemical mixture of N components, viz. $\varrho^\alpha(\boldsymbol{x}, t)$, with $\alpha = 1, 2, \ldots, N$ (cf. Chap. 3). To derive the respective field for a mixture with continuous diversity, one must simply allow the species label α to be no longer related to a finite enumerating set of N integer numbers, but rather to become a real number defined in a closed interval $[\alpha_{\min}, \alpha_{\max}] = \mathcal{A} \subset \mathbb{R}$, which is called the *species assemblage*. The extrema $\alpha_{\min}$ and $\alpha_{\max}$ are so defined as the assemblage $\mathcal{A}$ to be *complete*, i.e., it accounts for all possible species in the medium.

At first sight, the adoption of this new picture brings no dramatic changes in the description of the mixture. For instance, whatever the particular physical meaning given for α, the reference to any particle of the continuum, at a given time t, continues to be defined by the instantaneous position $\boldsymbol{x}$ of this particle and its constituent label α, exactly in the same way as in usual mixtures. However, the great difference is that the species label α is now continuous. In practice, this means that $\alpha \in \mathcal{A}$ acquired the status of a new variable, in addition to $\boldsymbol{x}$ and t, in such a way that the constituent mass density field in a mixture with continuous diversity reads $\varrho^*(\boldsymbol{x}, t, \alpha)$, where the superscript "$*$" indicates that the respective field is defined, for any given time t, in a space of dimension higher than three, namely the *space–assemblage* $\mathbb{R}^3 \times \mathcal{A}$. Of course, the same procedure can be extended to any other physical quantity of the medium, enabling so the definition of the constituent fields of stress $\mathbf{t}^*(\boldsymbol{x}, t, \alpha)$, specific internal energy $e^*(\boldsymbol{x}, t, \alpha)$, translational velocity $\boldsymbol{v}^*(\boldsymbol{x}, t, \alpha)$, etc.

There are some remarkable aspects of media with continuous diversity which deserve special attention. First, the theory is absolutely insensitive to the number of constituents. Indeed, while in a usual chemical mixture the amount of fields increases dramatically with the number of constituents, in a mixture with continuous diversity there occurs no change at all: it does not matter how much one enlarges the species assemblage $\mathcal{A}$, the number of fields of the theory remains always invariable (in the simplest case, just one field of mass density, one field of stress, etc.). This peculiarity of the theory represents a great benefit, for the size of the species assemblage can be freely chosen according to the necessities of the problem, without increasing of mathematical complexity. Second, as far as a physical meaning is attributed to the label α (for instance, size or orientation), an intrinsic hierarchy of constituents naturally emerges in the species assemblage $\mathcal{A}$. This hierarchy is characterized by the fundamental concept of *familiarity*, which is in fact the key to identify a medium as

a mixture with continuous diversity. Two species (i.e., constituents) are said *familiar* if their distinguishing properties – and consequently, their physical behavior – are alike, though not identical. The concept of familiarity is a direct consequence of the existence of a metric in the interval $\mathcal{A}$, and is the counterpart of the notion of closeness in the Euclidean space.

One of the great virtues of the notion of familiarity is that it allows one to treat the species label α and the position $\boldsymbol{x}$ at the same footing. Indeed, one can now even conceive a situation in which, besides usual mass changes due to transport phenomena, the mass density of constituent α varies in time through (inter-)species transitions. From the obvious similarity of these transitions with ordinary motions in the Euclidean space, we immediately conclude that the rate at which such continuous mutations occur can be described by a kind of "velocity", called *transition rate* $u^*(\boldsymbol{x}, t, \alpha)$. In fact, by considering a unit volume in a medium at rest ($v_i^* = 0$ for all points of the medium), it is easy to conclude that the quantity u^* determines the rate at which the amount of mass ϱ^* performs a continuous transition from constituent α to some other species, by altering its distinguishing properties. Note that the nature of such a transition is not restricted to any particular type of transformation, mutation, degradation or regeneration of the constituent properties. Nevertheless, it must be continuous. In other words, it must occur between *familiar species*.

Once the notion of interspecies transition rate is understood, it turns possible to talk about balance equations for mixtures with continuous diversity. There are essentially two ways of deriving such equations: the first, more formal, is by repeating the same arguments presented in Sect. 3.3, but now regarding a higher dimensional region $\mathcal{V} \times \mathcal{P} \subset \mathbb{R}^4$ (with $\mathcal{V} \subset \mathcal{B} \subset \mathbb{R}^3$ and $\mathcal{P} \subset \mathcal{A} \subset \mathbb{R}$); the second, on the other hand, is by direct extension of (3.19) to the case of a mixture with continuous diversity. This last approach will be now addressed here, while the first one is left to Chap. 6. The mentioned extension of (3.19) is performed in a similar manner as for the obtention of ϱ^* from ϱ^α. This procedure is straightforward for the time derivative, production and supply terms appearing in (3.19) and yields $\varrho^* \mathsf{a}^*$, $\varrho^* \mathsf{p}^*$ and $\varrho^* \mathsf{s}^*$. Nevertheless, a bit of care is needed when executing the extension of the flux terms of (3.19), owing to the dimension increase of the configuration space, viz. from $\mathbb{R}^3$ to $\mathbb{R}^4$. Effectively, this implies the conversion of coordinates $(x_i) \to (x_i, \alpha)$. Likewise, the velocity and conductive flux must obey similar conversions, namely $(v_i^\alpha) \to (v_i^*, u^*)$ and $(\mathsf{q}_i^\alpha) \to (\mathsf{q}_i^*, \mathsf{t}^*)$, where t^* represents an *interspecies conductive flux density* (in the species assemblage), or in other words, a *transmissive flux density*. Hence, from this rationale follows the local master balance equation (in regular points) for mixtures with continuous diversity

$$\frac{\partial \varrho^* \mathsf{a}^*}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^* \mathsf{a}^* v_i^* + \mathsf{q}_i^*\right) + \frac{\partial}{\partial \alpha}\left(\varrho^* \mathsf{a}^* u^* + \mathsf{t}^*\right) = \varrho^* \mathsf{p}^* + \varrho^* \mathsf{s}^* . \tag{5.1}$$

It must be emphasized that, in analogy to conductive fluxes (see Sect. 3.2), transmissive fluxes are defined by the absence of mass transport in $\mathcal{A}$, i.e., of interspecies transitions. Consequently, when deriving the mass balance equation for mixtures with continuous diversity, one must choose

a^*	q_i^*	t^*	p^*	s^*
1	0	0	Γ^*	0

$$\frac{\partial \varrho^*}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^* v_i^*\right) + \frac{\partial}{\partial \alpha}\left(\varrho^* u^*\right) = \varrho^* \Gamma^* \,, \tag{5.2}$$

which is named the *species balance equation of mass*.

At this moment it must be noticed that nothing was said yet about *mixture* fields, namely $\varrho(x_i, t)$, $v_i(x_j, t)$, etc. For consistence, these should be given by the mathematical counterparts of the sums (3.1) and (3.2) in a continuous interval of species, namely the integrals

$$\varrho = \int_{\mathcal{A}} \varrho^* \, \mathrm{d}\alpha \,, \qquad\qquad v_i = \frac{1}{\varrho} \int_{\mathcal{A}} \varrho^* v_i^* \, \mathrm{d}\alpha \,. \tag{5.3}$$

Hence, $v_i(x_j, t)$ is still the barycentric velocity of the mixture. Additionally, one concludes from (3.50) that the integral of the mass production $\varrho^* \Gamma^*$ over the whole species assemblage $\mathcal{A}$ must vanish, in concordance with the conservation of mass of the mixture. Finally, excluding for the moment the possibility of singularities in $\mathcal{A}$, it follows from the completeness assumed for the species assemblage that

$$\int_{\mathcal{A}} \frac{\partial}{\partial \alpha}\left(\varrho^* u^*\right) \, \mathrm{d}\alpha = 0 \,, \tag{5.4}$$

which simply reflects the fact that there are no species defined outside $\mathcal{A}$. Actually, (5.4) is a particular result of

Theorem 5.2.1 (completeness). *Under the condition that an arbitrary scalar, vector or tensor valued quantity $\mathsf{Q}^*(x_i, t, \alpha)$ is a continuously differentiable function of α in $\mathcal{A}$, and provided that the domain $\mathcal{A}$ is* complete*, i.e., that the species assemblage encloses* all *possible species of the medium, so that its extrema are fixed and maximized, then the following identity holds*

$$\int_{\mathcal{A}} \frac{\partial \mathsf{Q}^*}{\partial \alpha} \, \mathrm{d}\alpha = 0 \,. \tag{5.5}$$

The proof of this theorem becomes trivial, after one recognizes that the integrand of (5.5) represents in some sense the divergent of a "flux" within $\mathcal{A}$. Thence, since the species assemblage is complete, there cannot occur fluxes outside the interval. Mathematically, one must simply rewrite (5.5) as

$$\int_{\mathcal{A}} \frac{\partial \mathsf{Q}^*}{\partial \alpha} \, \mathrm{d}\alpha \;=\; \int_{\alpha_{\min}}^{\alpha_{\max}} \frac{\partial \mathsf{Q}^*}{\partial \alpha} \, \mathrm{d}\alpha \;=\; \frac{\partial}{\partial \alpha} \int_{\alpha_{\min}}^{\alpha_{\max}} \mathsf{Q}^* \, \mathrm{d}\alpha \;=\; \frac{\partial}{\partial \alpha} \mathsf{Q}_{\,\mathrm{int}}(x_i, t) = 0 \,, \tag{5.6}$$

where

$$\mathsf{Q}_{\,\mathrm{int}}(x_i, t) = \int_{\mathcal{A}} \mathsf{Q}^* \, \mathrm{d}\alpha \ , \tag{5.7}$$

where use was made of the assumed continuity of Q^* and the fact that, when $\mathcal{A}$ is complete, both extrema $\alpha_{\min}$ and $\alpha_{\max}$ are fixed (i.e., independent of α).

Evidently, from (5.2)–(5.4) one recovers the usual continuity equation (3.53), implying that the mixture behavior is that of a single medium.

Balance equations of momenta and energy will not be considered at this stage. different forms of such balance equations can occur, depending on the physical meaning specified for the variable α. Of course, in any case these equations must be compatible in form with (5.1).

5.3 Entropy principle

Before proceeding with thermodynamics, some remarks are appropriate here. For simplicity, throughout this chapter only one temperature field, the temperature of the mixture, will be considered. Accordingly, the main objective of the thermodynamic theory, viz., the prediction of the mixture behavior once the external agents are specified, reduces to the determination of the constituent fields of mass density, velocity and transition rate, as well as the temperature of the mixture (if no further fields are specified). Clearly, balance equations of mass, momenta and energy do not suffice for the determination of these fields, because they contain also additional fluxes and production terms which depend on the particularities of the medium. Hence, one must introduce supplementary hypotheses, in order to relate these additional quantities to the basic fields of the theory, through the so called *constitutive relations*. Nonetheless, these relations cannot be arbitrary. They must satisfy some fundamental physical axioms, among them the entropy principle.

The results presented up to now provide a solid background for the formulation of an entropy principle appropriate for mixtures with continuous diversity. Actually, no modification of the classical version of this principle is necessary for the mixture as a whole, i.e., (3.60) remains valid. Nevertheless, in contrast to the usual theory of mixtures, an entropy inequality in the form (3.60) is somewhat unworthy for a constitutive theory in the space–assemblage. In fact, the standard method of exploitation of the entropy principle via Lagrange multipliers, as proposed by Liu [274], is no longer applicable in such a situation. The reason is that the algebraic equivalence on which the whole method is founded cannot be justified, in this case, by customary arguments.

The admissibility of the method of Lagrange multipliers has become a very desirable feature for any thermodynamic theory of continua. In fact, the use of Lagrange multipliers makes the exploitation of the entropy principle not only a systematic and straightforward procedure, but also equivalent to the maximization of entropy in non-equilibrium (see [107]). Therefore, in order to confer such a pleasant feature to the theory developed here, one has two alternatives: the first could be the derivation of a new version of the method of Lagrange multipliers, by introducing multiplier

functions in integral form; the second would require a reformulation of the entropy principle in space–assemblage, which should be compatible with the conventional form of the Lagrange multiplier method. The second option has been addressed in [129] and is discussed below; the first one remains open for mathematicians.

In order to define an entropy principle appropriate for mixtures with continuous diversity, it is sufficient to rephrase (with only some slight modifications) the axiomatic formulation of Müller [317]. It will be stated here in three parts:

Postulate 5.3.1 (Entropy principle).

1. *There exists for each component of the mixture an additive scalar quantity, the entropy of the species α.*
2. *The specific entropy, the entropy fluxes and the specific entropy production of each component of the mixture are given by constitutive equations.*
3. *The entropy production of the mixture is non-negative for all thermodynamic processes.*

From the first axiom follows, with the help of (5.1), the species entropy balance equation in the form

a^*	q_i^*	t^*	p^*	s^*
η^*	ϕ_i^*	φ^*	ς^*	s^*

$$\frac{\partial \varrho^* \eta^*}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^* \eta^* v_i^* + \phi_i^*\right) + \frac{\partial}{\partial \alpha}\left(\varrho^* \eta^* u^* + \varphi^*\right) = \varrho^* \varsigma^* + \varrho^* s^*, \tag{5.8}$$

where η^* is the species specific entropy, ϕ_i^* and φ^* its fluxes, ς^* its specific production and s^* its external supply. According to the second axiom, all these fields (but the last, which is defined by external conditions) are given by constitutive functions. Note also that, from $(3.43)_3$, $(3.45)_2$, (3.49) and the third axiom,

$$\eta = \frac{1}{\varrho}\int_{\mathcal{A}} \varrho^* \eta^* \, \mathrm{d}\alpha \,, \qquad \phi_i = \int_{\mathcal{A}} \left(\phi_i^* + \varrho^* H^* C_i^*\right) \,, \tag{5.9}$$

$$s + \varsigma = \frac{1}{\varrho}\int_{\mathcal{A}} \varrho^* \left(s^* + \varsigma^*\right) \mathrm{d}\alpha \qquad \text{and} \qquad \varsigma \geq 0 \,, \tag{5.10}$$

with

$$C_i^* = v_i^* - v_i \,, \qquad H^* = \eta^* - \eta \,. \tag{5.11}$$

In particular, with respect to an inertial referential, (5.10) reduces to (cf.

$$s = \frac{1}{\varrho}\int_{\mathcal{A}} \varrho^* s^* \, \mathrm{d}\alpha \,, \qquad \text{and} \qquad \varsigma = \frac{1}{\varrho}\int_{\mathcal{A}} \varrho^* \varsigma^* \, \mathrm{d}\alpha \geq 0 \,. \tag{5.12}$$

It should be observed that, in any case, the production ς^* can also assume negative values, caused by the influence of the other components present in the mixture. One

can exclude for a while such intricate influences by considering the limiting case when all constituents are absent but one, i.e., a one-component continuum. In such a simple situation, the specific entropy production of the pure constituent would be given simply by

$$\varsigma^{*\mathrm{P}} \geq 0, \tag{5.13}$$

as obviously should be for a single medium.

Consequently, returning to the general case, one can define for every component of the mixture, a deviation measure of the constituent entropy production from its expected behavior in a single medium by

$$\delta^* = \varsigma^* - \varsigma^{*\mathrm{P}}, \tag{5.14}$$

which will be called the entropy production deviation due to constituent interactions, or for short, *entropy production deviation.*

Once ς^* is a constitutive function (due to the second axiom of the entropy principle), so is $\varsigma^{*\mathrm{P}}$. Accordingly, from (5.14) there follows that the deviation function $\delta^*(x_i, t, \alpha)$ must also be a constitutive quantity. These results, combined with the inequality (5.13), complete the proof of

Theorem 5.3.1 (δ^*). *There exists a function*

$$\delta^* : \mathbb{R}^4 \times \mathcal{A} \to \mathbb{R}\ ,$$

defined through (5.14), *which is given by a constitutive equation and such that, with reference to an inertial observer, the inequality*

$$\varsigma^* \geq \delta^* \tag{5.15}$$

holds for all thermodynamic processes.

This theorem is the most prominent result of the theory, and enables the entropy principle to be expressed in the space–assemblage. In simple words, it guarantees the existence of the deviation function $\delta^*(x_i, t, \alpha)$ and asserts that it is a constitutive quantity whose value is upper-bounded by the constituent entropy production for any thermodynamic process. The extension of (5.15) to non-inertial reference frames depends on the validity of (5.12) for such cases. Indeed, as demonstrated in Chap. 4, the conservation of angular momentum and energy might sometimes assume more complicated forms, when referred to non-inertial observers (cf. (4.34), (4.35) and (4.39)). Accordingly, one could also cogitate the possibility that, for some particular microstructured mixture, (5.12) could eventually fail to hold in a non-inertial frame of reference, even though (5.10) necessarily remains valid.

It is worth noticing that the δ^*-theorem can be automatically applied to ordinary mixtures too, for which (5.14) and (5.15) are simply replaced by

$$\delta^\alpha = \varsigma^\alpha - \varsigma^{\alpha\mathrm{P}}\ , \qquad \text{and} \qquad \varsigma^\alpha \geq \delta^\alpha\ , \tag{5.16}$$

where ς^α and $\varsigma^{\alpha\mathrm{P}}$ represent respectively the specific entropy production of the constituent α in the mixture and in a pure state. It must be emphasized, however, that

a constituent entropy inequality of the form (5.16) is for most situations unnecessary, for it simply complicates the exploitation of the second law of thermodynamics, which for ordinary mixtures can be readily performed using the mixture entropy inequality $(5.10)_2$. It is instructive to remark that former authors had also attempted to construct entropy inequalities for the constituents of a mixture, but in vain. As a matter of fact, in most approaches (see e.g. [124]) the constituent entropy production ς^α was assumed to be decomposed into two additive parts, one representing a non-negative "real" production of entropy by the α-constituent ($\varsigma^{\alpha_{\mathrm{R}}}$) and another one expressing a globally reversible entropy production by constituent interactions and chemical reactions ($\varsigma^{\alpha_{\mathrm{I}}}$), viz.

$$\varsigma^\alpha = \varsigma^{\alpha_{\mathrm{R}}} + \varsigma^{\alpha_{\mathrm{I}}} \qquad \text{with} \qquad \varsigma^{\alpha_{\mathrm{R}}} \geq 0 \,, \qquad \sum_{\alpha=1}^{N} \varrho^\alpha \varsigma^{\alpha_{\mathrm{I}}} = 0 \,. \tag{5.17}$$

Definition (5.17) is evidently doomed to fail, not only in view of the fact that $(5.17)_2$ is obviously wrong, but also because the assumption that the "real" production $\varsigma^{\alpha_{\mathrm{R}}}$ is not affected by the presence of other constituents is – at least – very questionable[2].

In contrast, no attempt to resolve the entropy production into distinct terms is made in the definitions (5.14) and (5.15) or (5.16). Therefore, ς^* (or ς^α) remains completely arbitrary, as far as (5.10) is satisfied. The entropy inequality (5.15) is derived by *introducing an additional concept*, rather than making restrictive assumptions upon already existing terms. This new concept, the entropy production deviation, relates the entropy production of a constituent in the mixture to its counterpart in an equivalent single medium (pure constituent). Such a sort of relationship between mixture and pure constituents is by no means wondrous or bizarre: actually it can be frequently found in chemistry, as in the definition of chemical potential or in the laws of Raoult and Henry [96, 144, 191, 271, 307].

5.4 Extension for the case of multi-labelled species

The generalization of the mixture theory presented in the last section is still not able to deal with many of the common mixtures with continuous diversity found in nature. In fact, the identification of a particular species requires in many situations the specification of more than one distinctive property. A simple example is the gas with non-spherical molecules considered by Curtiss [84], where any species is identified by two parameters, related to the azimuthal and the polar orientation angles, respectively. Therefore, following the motto "*when we start to generalize, it is hard to know when to stop*" (Truesdell [406], p. 24) (cf. Sect. 2.3), a trivial extension

[2]Imagine for instance a class of children playing for a while alone in a dark classroom and, consequently, producing a lot of entropy there. When the angry teacher silently comes in and punishes one of the children, who cries, all the others immediately start to behave in a different way, even though the interaction occurred solely with one child and the others do not know exactly what has happened. Hence, the knowledge of the presence of another "constituent" (the teacher) was transmitted through the "medium" by one child to the others, without necessity of direct interaction of the adult with *every* child. Consequently, when mixed with teachers, children behave differently. In a chemical mixture, one could easily conceive a similar situation.

of the theory presented in the last Section, valid for the case of multi-labelled species, will now be derived.

Consider first that every component of the mixture is identified with a set of continuous labels α_I $(I = 1, 2, \ldots, M)$, each one defined in a particular closed interval $\mathcal{A}_I \subset \mathbb{R}$. Hence, the space–assemblage assumes the multi-dimensional form $(\mathbb{R}^3 \times \mathcal{M}) \subset \mathbb{R}^{M+3}$, where $\mathcal{M} = \mathcal{A}_1 \times \mathcal{A}_2 \times \cdots \times \mathcal{A}_M$.

Accordingly, the master balance equation appropriate for the case of multi-labelled species remains essentially identical in form to (5.1), but now the derivative with respect to α assumes the form of a kind of "divergence operator" in the species assemblage $\mathcal{M}$, viz.

$$\frac{\partial \varrho^* \mathsf{a}^*}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^* \mathsf{a}^* v_i^* + \mathsf{q}_i^*\right) + \frac{\partial}{\partial \alpha_I}\left(\varrho^* \mathsf{a}^* u_I^* + \mathsf{t}_I^*\right) = \varrho^* \mathsf{p}^* + \varrho^* \mathsf{s}^* , \tag{5.18}$$

with the evident summation convention of the dummy indices $i = 1, 2, 3$ and $I = 1, 2, \ldots, M$.

Provided that all the essential assumptions considered in Sects. 5.2 and 5.3 remain valid, it is straightforward to derive the extended version of the theory, by trivial replacement of α, u^*, t^* and $\mathcal{A}$ in equations (5.2)–(5.15) respectively by α_I, u_I^*, t_I^* and $\mathcal{M}$. For instance, the mass balance equation (5.2) and the expressions (5.3) are rewritten in this case as

$$\frac{\partial \varrho^*}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^* v_i^*\right) + \frac{\partial}{\partial \alpha_I}\left(\varrho^* u_I^*\right) = \varrho^* \Gamma^* , \tag{5.19}$$

$$\varrho = \int_{\mathcal{M}} \varrho^* \, \mathrm{d}^M\alpha , \qquad \text{and} \qquad v_i = \frac{1}{\varrho}\int_{\mathcal{M}} \varrho^* v_i^* \, \mathrm{d}^M\alpha , \tag{5.20}$$

where the following notation was adopted:

$$\int_{\mathcal{M}} \mathsf{Q}^* \, \mathrm{d}^M\alpha = \int_{\mathcal{A}_1}\int_{\mathcal{A}_2} \cdots \int_{\mathcal{A}_M} \mathsf{Q}^* \, \mathrm{d}\alpha_M \ldots \mathrm{d}\alpha_2 \mathrm{d}\alpha_1 .$$

Furthermore, the completeness theorem (5.2.1) takes the form

$$\int_{\mathcal{M}} \frac{\partial \mathsf{Q}_I^*}{\partial \alpha_I} \, \mathrm{d}^M\alpha = 0 , \tag{5.21}$$

for any continuously differentiable vector field Q_I^* on $\mathcal{M}$.

From the considerations above, the vectorial character achieved by the label α_I, the transmissive flux density t_I^* and the transition rate u_I^* becomes now clear. As remarked by Condiff & Brenner [78], this vectorial character is a fundamental feature in the study of anisotropic media.

Finally, keeping in mind also that, in such a generalized case, all thermodynamic fields are defined for every time t in the hyperspace $\mathbb{R}^3 \times \mathcal{M}$, no further modification of the entropy principle and δ^*-theorem (respectively Postulate 5.3.1 and Theorem 5.3.1), as presented in the last section, is necessary. Therefore, the extension of the theory is complete[3].

[3] Of course, an "hybrid" version of the theory could also be obtained by mixing continuous and discrete distinctive properties. This will be considered in the next Chapter.

6. Mixtures of Microstructured Media: Quintessential Examples of Hybrid Mixtures with Continuous Diversity

I judge it the second step by which the Pyramid of natural knowledge (which is the knowledge of the form of bodies) is to be ascended: And whosoever will climb it, must be well furnished with that which the Noble Verulam calls Scalam Intellectus; he must have scaling Ladders, otherwise the steps are so large and high, there will be no getting up them, and consequently little hopes of attaining any higher station, [...]; for it seems tome, that the Intellect of man is like his body, destitute of wings, and cannot move from a lower to a higher and more sublime station of knowledge, otherwise then step by step, nay even there where the way is prepared and already made passible; as in the Elements of Geometry, or the like, where it is fain to climb a whole series of Propositions by degrees, before it attains the knowledge of one Probleme. But if the ascent be high, difficult and above its reach, it must have recourse to a novum organum, some new engine and contrivance, some new kind of Algebra, or Analytick Art before it can surmount it.

Robert Hooke, [215] p. 93

The concept of microstructured medium immediately suggests the existence of some kind of "underlying bricks" which build the microstructure of the material. Such "bricks", called *primitive microstructural elements*, may be of diverse nature, like crystallites of a polycrystal, grains in a granular material, floes of a sea ice pack and macromolecules in a polymeric solution. Accordingly, mixtures of such microstructured media encompass solid solutions, polycrystalline alloys, composites, complex suspensions and polydisperse granular media, among others. The subject matter of this Chapter are those types of chemically reacting mixtures of microstructured media whose primitive microstructural elements possess uniaxial symmetry. Full sets of balance equations and jump conditions are derived for single and mixed continua, which are appropriate for a wide range of applications, from the creep of polycrystals to the flow of granular media and chemically reacting macromolecular solutions. Thanks to the use of the framework of mixtures with continuous diversity discussed in Chap. 5, both isotropic and anisotropic media can be considered at the same footing and some interesting effects, like net *orientational* diffusive fluxes of mass, are predicted.

6.1 Doubly complex media

Since the birth of continuum mechanics and thermodynamics as a branch of science, the most acknowledged connection between chemical mixtures and microstructured continua has been their common and obscure classification as "complex media". Actually, such a complexity is mainly caused by internal processes and interactions on the meso- and microscopic levels, which cannot be captured through an ordinary continuum formalism. In spite of this elementary kinship, the development of thermodynamic theories for mixtures followed a quite distinct way from that trailed by theories for microstructured continua. Meaningful concepts from chemistry, statistical physics and kinetic theory assisted the unified campaign towards the construction of a definite and rather general theory of mixtures [51, 115, 178, 240, 405], which achieved its acme with the work of Müller [315] (see also [316]; a historical survey is available in [14]). On the other hand, the thermodynamics of microstructured media evolved in a similarly elegant (though more mathematical) environment, while it did never experience the same integrate engagement as found for chemical mixtures. Indeed, many different approaches to microstructured continua have appeared [6, 46, 82, 87, 88, 125, 179], as can be well exemplified by the several names for the microstructural angular velocity found in the literature: rotary velocity, lattice spin, spin velocity (or simply spin), gyration and intrinsic angular velocity, among others.

Possibly due to the fear of facing a "complex medium to the square power" the scientific literature on chemically reacting mixtures of microstructured media has remained very scarce, the most noticeable contributions being due to Kelly [240], Allen & Kline [7] and Twiss & Eringen [411] (see Chap. 3). A former phenomenological approach was also presented by Condiff & Brenner [78], albeit without the deserved repercussion, probably because of the old-fashioned background on thermodynamics of irreversible processes presented there. This is nevertheless a work of great originality, based on a physically appealing picture of the microstructure as a "mixture of orientations". Such a picture has its origins in earlier results from kinetic and statistical theories, as those evidenced in the works of Prager [354] and Curtiss [84], which were extended and generalized in the notable treatise of Dahler [85]. Supported by the legacy of these four seminal studies, as well as by other theories in the branches of chemistry, rheology, geophysics and biomathematics (e.g. [11, 43, 46, 149, 166, 207, 320, 372, 432]), a thermodynamic theory for *mixtures with continuous diversity* has been recently proposed [129, 132] (see Chap. 5), which consists of a general continuum framework to deal with most of such once called "complex media".

While Condiff & Brenner [78] and Faria [129] have illustrated how concepts from mixture theory could be useful in the understanding of microstructured media (by analyzing the flow-induced anisotropy of some polymeric solutions), in the present Chapter (see also [132]) the opposite situation is discussed, namely how the physics of microstructured media, modeled as mixtures with continuous diversity, can enlighten new issues in the theory of mixtures.

In contrast to Chap.4, where mixtures of a particular type of microstructured medium – namely, liquid crystals – have already been considered, no director field is implemented here. Instead, the theory of mixtures with continuous diversity discussed in Chap. 5 is employed, permitting so the regard of structured media with any degree of order, from isotropic to highly anisotropic. For explicitness, the primitive microstructural elements are assumed to possess *uniaxial symmetry*, defined for instance by the c-axis of a crystallite with hexagonal symmetry or the long axis of a rigid axisymmetric macromolecule in suspension; nevertheless, the symmetry of the mixture itself remains fully unconstrained.

6.2 Identifying species and constituents

In the case of single media, the basic hypothesis of the theory of mixtures with continuous diversity is that the material response of a microstructured medium depends on the amount of matter oriented into different directions in the same way as the material response of an ordinary chemical mixture depends on the concentration of its constituents.

Mathematically, one means of describing orientations in space is by associating them with points of $\mathcal{S}^2 \subset \mathbb{R}^3$, which is envisaged as a closed spherical surface of unit radius embedded in $\mathbb{R}^3$ [1] (see Fig.6.1). In principle, any point of $\mathcal{S}^2$ could be identified by its spherical (polar and azimuthal) angles, viz, θ and φ. Nevertheless, since these angles define a unique direction in $\mathbb{R}^3$ and calculations using spherical coordinates are rather cumbersome, it is more convenient to associate θ and φ to the Cartesian components of the normalized *orientation vector* $n_i \in \mathbb{R}^3$ (with $n_i n_i = 1$), which is nothing else than the unit radius vector of the spherical surface of $\mathcal{S}^2$ in $\mathbb{R}^3$. Therefore, $\mathcal{S}^2$ is also referred to as the *orientation space*. Now, as long as the primitive microstructural elements of the considered media possess uniaxial symmetry, it becomes clear that the appropriate identification of a species is accomplished by the adoption of two species labels, associated to the two independent Cartesian components of the orientation vector n_i, building so the picture of a "mixture of orientations". Such a picture has been exploited in the literature of single media for some particular materials, like liquid crystals [46], polymeric solutions [129], polyatomic gases [84, 85], polycrystalline ice [166] and granular materials [118].

On the other hand, the extension of these ideas for multicomponent media is scarce [78, 132]. In principle, the basic difference is that one must deal with N distinct "mixtures of orientations", consequently requiring the incorporation of an additional

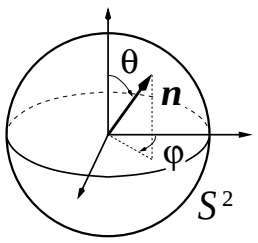


Fig. 6.1. Relationship between the orientation $\boldsymbol{n}$ and its characteristic angles, θ and φ. $\mathcal{S}^2$ is the orientation space

species label $\alpha = 1, 2, \ldots, N$ to identify the individual chemical constituents. In other words, a *hybrid* mixture with continuous diversity emerges, involving simultaneously discrete (α) and continuous (n_i) species labels.

From the discussion at the beginning of Sect. 5.3 and the reasoning above, it follows that the thermodynamic description of microstructured mixtures commonly involves the determination of $8N$ orientation dependent fields for the constituents, viz.[1] ($\alpha = 1, 2, \ldots, N$)

$$\begin{aligned} &\text{mass density} && \varrho^{*\alpha}(x_i, t, n_j)\ , \\ &\text{specific linear momentum (translational velocity)} && v_i^{*\alpha}(x_j, t, n_k)\ , \\ &\text{specific spin} && \sigma_i^{*\alpha}(x_j, t, n_k)\ , \\ &\text{specific internal energy} && e^{*\alpha}(x_i, t, n_j)\ , \end{aligned} \tag{6.1}$$

all defined in the domain $\mathcal{B} \times \mathcal{T} \times \mathcal{S}^2 \subset \mathbb{R}^6$, where $\mathcal{B} \subset \mathbb{R}^3$ and $\mathcal{T} \subseteq \mathbb{R}^1$ are the body and time manifolds (see App. A).

It is of fundamental importance to understand that n_i is *not* a material vector, i.e., it is not fixed to the microstructure, as in the case of Cosserat continua. It just defines a direction in space. Consequently, when the symmetry axis of some microstructural element rotates, it does not carry the vector n_i with it. On the contrary, this axis simply changes its orientation from n_i to another one, in a similar way as the center of mass of a particle changes its position x_i by translation. Therefore, in this sense it can be stated that the description adopted here is *spatial* in both, the orientation and the Euclidean spaces.

The occurrence of two superscripts ($*$ and α) in (6.1) implicitly indicates the existence of four levels of description of the microstructure. Effectively, if Q denotes an arbitrary scalar, vector or tensor valued quantity, then

- ❶ $\mathsf{Q}^{*\alpha} = \mathsf{Q}^{*\alpha}(x_i, t, n_j)$ is its orientation dependent field for constituent α,
- ❷ $\mathsf{Q}^{\alpha} = \mathsf{Q}^{\alpha}(x_i, t)$ is its field for constituent α,
- ❸ $\mathsf{Q}^{*} = \mathsf{Q}^{*}(x_i, t, n_j)$ is its orientation dependent field (for the mixture),
- ❹ $\mathsf{Q} = \mathsf{Q}(x_i, t)$ is its field (for the mixture).

Furthermore, all the description levels listed above can be simultaneously represented by the generic notation $\mathsf{Q}^{\cdots}$.

Once the rules for identification of species and constituents are defined and the multiple levels of description of the mixture are recognized, there remains to perform just a straightforward generalization of the procedures thoroughly discussed

[1] As usual in thermodynamic applications, it can be sometimes advantageous to consider some more specialized set of thermodynamic fields than (3.24). The most common situation occurs when a single temperature for all chemical constituents and orientations is allowed. In this case one could, for instance, substitute the N orientation dependent fields of internal energy of the constituents $e^{*\alpha}(x_i, t, n_j)$ by just one field of absolute temperature $T(x_i, t)$, provided an appropriate thermal equation of state exists. This simplifies the thermodynamic description of such media to the determination of $7N + 1$ fields.

for ordinary chemical mixtures in Chap. 3, in order to derive the appropriate balance equations for single- and multicomponent microstructured media. The transition from ordinary mixtures to mixtures with continuous diversity has been outlined in Chap: 5. Hence, the next sections will be, roughly, a blend of these two Chapters. In particular, a conspicuous similarity will be intentionally promoted between the structure of Chap. 3 and the present Chapter in order to facilitate the analogy between these two types of mixtures.

Consequently, the starting point of this study is again the definition of mixture as a superposition of N continuous bodies $\mathcal{B}^\alpha$ ($\alpha = 1, 2, \ldots, N$), all able to occupy simultaneously the same region of space. The superposed bodies constitute thence the mixture body $\mathcal{B}$. Accordingly, the mass density of the mixture $\varrho(x_i, t)$ is again defined as the sum, over all α, of the mass densities of the constituents $\varrho^\alpha(x_i, t)$, as expressed in (3.1). The difference now is that every chemical constituent is in fact a microstructured medium modeled as a mixture with continuous diversity. Also, in harmony with $(5.3)_1$, the mass density of the α-th chemical constituent is defined as

$$\varrho^\alpha = \oint_{\mathcal{S}^2} \varrho^{*\alpha}\, \mathrm{d}^2 n\ , \qquad \text{and consequently} \qquad \varrho = \sum_{\alpha=1}^{N} \oint_{\mathcal{S}^2} \varrho^{*\alpha}\, \mathrm{d}^2 n\ . \tag{6.2}$$

Of course, the order of summation and integration can be reversed in $(6.2)_2$, leading to the definition

$$\varrho^* = \sum_{\alpha=1}^{N} \varrho^{*\alpha}\ , \qquad \text{while} \quad (5.3)_1 \ \text{remains valid.} \tag{6.3}$$

Thus, it becomes clear that one can easily move from one level of description to another by playing with the order of sums and integrals. Indeed, the same holds also for the barycentric translational velocity of the mixture, which can be calculated in different ways with the aid of (3.2), $(5.3)_2$ and

$$v_i^\alpha = \frac{1}{\varrho^\alpha} \oint_{\mathcal{S}^2} \varrho^{*\alpha} v_i^{*\alpha}\, \mathrm{d}^2 n\ , \qquad v_i^* = \frac{1}{\varrho^*} \sum_{\alpha=1}^{N} \varrho^{*\alpha} v_i^{*\alpha}\ , \qquad v_i = \frac{1}{\varrho} \sum_{\alpha=1}^{N} \oint_{\mathcal{S}^2} \varrho^{*\alpha} v_i^{*\alpha}\, \mathrm{d}^2 n\ . \tag{6.4}$$

Moreover, there exist in this situation five different relative (diffusive) velocities, viz. (cf. (3.3) and (5.11))

$$\begin{gathered} C_i^{\underline{*}\alpha} = v_i^{*\alpha} - v_i^*, \qquad C_i^{*\underline{\alpha}} = v_i^{*\alpha} - v_i^\alpha, \qquad C_i^{*\alpha} = v_i^{*\alpha} - v_i, \\ C_i^* = v_i^* - v_i, \qquad C_i^\alpha = v_i^\alpha - v_i. \end{gathered} \tag{6.5}$$

Of course, from (6.4) and (6.5) follow

$$\sum_{\alpha=1}^{N} \varrho^{*\alpha} C_i^{\underline{*}\alpha} = 0 = \sum_{\alpha=1}^{N} \varrho^\alpha C_i^\alpha\ , \qquad \oint_{\mathcal{S}^2} \varrho^{*\alpha} C_i^{*\underline{\alpha}}\, \mathrm{d}^2 n = 0 = \oint_{\mathcal{S}^2} \varrho^* C_i^*\, \mathrm{d}^2 n\ , \tag{6.6}$$

$$\oint_{\mathcal{S}^2} \varrho^{*\alpha} C_i^{*\alpha}\, \mathrm{d}^2 n = \varrho^\alpha C_i^\alpha\ , \qquad \sum_{\alpha=1}^{N} \varrho^{*\alpha} C_i^{*\alpha} = \varrho^* C_i^*\ . \tag{6.7}$$

6.3 All those fluxes...

In Sect. 3.2, three fundamental sorts of flux have been studied: convective, diffusive and conductive fluxes. Yet, for the case of a "mixture of media with continuous diversity", three additional kinds of flux may arise, owing to the accretion of the $\mathcal{S}^2$ space. These are generically called *orientational* fluxes, and comprise transitional (or orientational convective), orientational diffusive and transmissive (or orientational conductive) fluxes.

Effectively, let $\mathcal{W}$ denote a (piecewise) smooth oriented surface moving with velocity $v_i^{\mathcal{W}}(x_j,t)$ within a region $\mathcal{V}\subset\mathcal{B}$. Assuming for a moment that all thermodynamic fields are continuous through the surface, it follows that the flux across $\mathcal{W}$ of an arbitrary additive quantity A, for any chemical constituent α and orientation n_i, can be easily derived from the expressions

$$\mathsf{F}^{*\alpha}(\mathcal{W},t,n_i)=\int\limits_{\mathcal{W}}\left(\mathsf{q}_i^{*\alpha}+\mathsf{f}_i^{*\alpha}\right)e_i^{\mathcal{W}}\,\mathrm{d}^2x,\qquad\qquad \mathsf{f}_i^{*\alpha}=\varrho^{*\alpha}\mathsf{a}^{*\alpha}\left(v_i^{*\alpha}-v_i^{\mathcal{W}}\right),\tag{6.8}$$

where $e_i^{\mathcal{W}}$ stands for the unit vector normal to $\mathcal{W}$ and $\varrho^{*\alpha}\mathsf{a}^{*\alpha}$ denotes the density field of $\mathsf{A}^{*\alpha}$, while $\mathsf{q}_i^{*\alpha}$ is its conductive flux density. Furthermore, the field $\mathsf{f}_i^{*\alpha}$ may represent either a convective flux (when $v_i^{\mathcal{W}}=0$) or a diffusive flux (when $v_i^{\mathcal{W}}=v_i$), as discussed in Situations (a) and (b) of Sect. 3.2.

The case of diffusive flux described by Situation (b) is of particular interest, so that the instance in which the surface $\mathcal{W}$ is material will be now analyzed in more detail. In such a circumstance, (6.8) yields

$$\mathsf{F}^{*\alpha}(\mathcal{W},t,n_i)=\int\limits_{\mathcal{W}}\left(\mathsf{q}_i^{*\alpha}+\varrho^{*\alpha}\mathsf{a}^{*\alpha}C_i^{*\alpha}\right)e_i^{\mathcal{W}}\,\mathrm{d}^2x\;,\tag{6.9}$$

in which one clearly recognizes its conductive ($\mathsf{q}_i^{*\alpha}$) and diffusive ($\varrho^{*\alpha}\mathsf{a}^{*\alpha}C_i^{*\alpha}$) parts. Following the same arguments leading to (3.9), one can introduce the orientational and constituent fluxes of the arbitrary additive quantity A respectively by

$$\begin{aligned}\mathsf{F}^{*}(\mathcal{W},t,n_i)\;=\sum_{\alpha=1}^{N}\mathsf{F}^{*\alpha}\;&=\sum_{\alpha=1}^{N}\int\limits_{\mathcal{W}}\left(\mathsf{q}_i^{*\alpha}+\varrho^{*\alpha}\mathsf{a}^{*\alpha}C_i^{*\alpha}\right)e_i^{\mathcal{W}}\,\mathrm{d}^2x\\&=\int\limits_{\mathcal{W}}\sum_{\alpha=1}^{N}\left(\mathsf{q}_i^{*\alpha}+\varrho^{*\alpha}\mathsf{a}^{*\alpha}C_{\bar{i}}^{*\alpha}+\varrho^{*}\mathsf{a}^{*}C_i^{*}\right)e_i^{\mathcal{W}}\,\mathrm{d}^2x\\&=\int\limits_{\mathcal{W}}\left(\mathsf{q}_i^{*}+\varrho^{*}\mathsf{a}^{*}C_i^{*}\right)e_i^{\mathcal{W}}\,\mathrm{d}^2x\;,\end{aligned}\tag{6.10}$$

and

$$
\begin{aligned}
\mathsf{F}^{\alpha}(\mathcal{W},t) \;=\; \oint_{\mathcal{S}^2}\mathsf{F}^{*\alpha}\,\mathrm{d}^2n \;&=\; \oint_{\mathcal{S}^2}\int_{\mathcal{W}}(\mathsf{q}_i^{*\alpha}+\varrho^{*\alpha}\mathsf{a}^{*\alpha}C_i^{*\alpha})\,\mathrm{e}_i^{\mathcal{W}}\,\mathrm{d}^2x\,\mathrm{d}^2n\\
&=\int_{\mathcal{W}}\oint_{\mathcal{S}^2}(\mathsf{q}_i^{*\alpha}+\varrho^{*\alpha}\mathsf{a}^{*\alpha}C_i^{*\underline{\alpha}}+\varrho^{\alpha}\mathsf{a}^{\alpha}C_i^{\alpha})\,\mathrm{e}_i^{\mathcal{W}}\,\mathrm{d}^2n\,\mathrm{d}^2x\\
&=\int_{\mathcal{W}}(\mathsf{q}_i^{\alpha}+\varrho^{\alpha}\mathsf{a}^{\alpha}C_i^{\alpha})\,\mathrm{e}_i^{\mathcal{W}}\,\mathrm{d}^2x\;, \qquad (6.11)
\end{aligned}
$$

with

$$
\begin{aligned}
\mathsf{q}_i^{*} &= \sum_{\alpha=1}^{N}(\mathsf{q}_i^{*\alpha}+\varrho^{*\alpha}\mathsf{a}^{*\alpha}C_i^{\underline{*}\alpha})\;, \qquad (6.12)\\
&= \sum_{\alpha=1}^{N}(\mathsf{q}_i^{*\alpha}+\varrho^{*\alpha}\mathsf{D}^{\underline{*}\alpha}C_i^{\underline{*}\alpha})\;, \qquad (6.13)
\end{aligned}
$$

and

$$
\begin{aligned}
\mathsf{q}_i^{\alpha} &= \oint_{\mathcal{S}^2}(\mathsf{q}_i^{*\alpha}+\varrho^{*\alpha}\mathsf{a}^{*\alpha}C_i^{*\underline{\alpha}})\,\mathrm{d}^2n\;, \qquad (6.14)\\
&= \oint_{\mathcal{S}^2}(\mathsf{q}_i^{*\alpha}+\varrho^{*\alpha}\mathsf{D}^{*\underline{\alpha}}C_i^{*\underline{\alpha}})\,\mathrm{d}^2n\;, \qquad (6.15)
\end{aligned}
$$

where (6.13) and (6.15) are derived under the assumption that (owing to the additivity of A)

$$
\mathsf{a}^{*}=\frac{1}{\varrho^{*}}\sum_{\alpha=1}^{N}\varrho^{*\alpha}\mathsf{a}^{*\alpha}\qquad\text{and}\qquad\mathsf{a}^{\alpha}=\frac{1}{\varrho^{\alpha}}\oint_{\mathcal{S}^2}\varrho^{*\alpha}\mathsf{a}^{*\alpha}\,\mathrm{d}^2n\;, \qquad (6.16)
$$

enabling so the introduction of the relative quantities

$$
\mathsf{D}^{\underline{*}\alpha}=\mathsf{a}^{*\alpha}-\mathsf{a}^{*}\qquad\text{and}\qquad\mathsf{D}^{*\underline{\alpha}}=\mathsf{a}^{*\alpha}-\mathsf{a}^{\alpha}\;. \qquad (6.17)
$$

Accordingly, the conductive flux density of the mixture can be derived either by integrating (6.10) on $\mathcal{S}^2$, or through summation of (6.11) over all α, yielding

$$
\begin{aligned}
\mathsf{q}_i \;&=\; \sum_{\alpha=1}^{N}(\mathsf{q}_i^{\alpha}+\varrho^{\alpha}\mathsf{D}^{\alpha}C_i^{\alpha})\,, \qquad (6.18)\\
&=\; \oint_{\mathcal{S}^2}(\mathsf{q}_i^{*}+\varrho^{*}\mathsf{D}^{*}C_i^{*})\,\mathrm{d}^2n\;, \qquad (6.19)\\
&=\; \oint_{\mathcal{S}^2}\sum_{\alpha=1}^{N}(\mathsf{q}_i^{*\alpha}+\varrho^{*\alpha}\mathsf{D}^{*\alpha}C_i^{*\alpha})\,\mathrm{d}^2n\;, \qquad (6.20)
\end{aligned}
$$

with D^{α} defined in (3.11), while

$$\mathsf{D}^* = \mathsf{a}^* - \mathsf{a}\ , \qquad \mathsf{D}^{*\alpha} = \mathsf{a}^{*\alpha} - \mathsf{a} \qquad \mathsf{a} = \frac{1}{\varrho}\oint\limits_{\mathcal{S}^2} \varrho^{*\alpha}\mathsf{a}^{*\alpha}\,\mathrm{d}^2 n\ . \tag{6.21}$$

As commented at the beginning of this Section, in addition to ordinary "spatial" fluxes one can also consider the additional orientational fluxes taking place in $\mathcal{S}^2$. The meaningful kinetic field in this case is the spin velocity $s_i^{*\alpha}$, or more directly the transition rate $u_i^{*\alpha}$, which plays the role of a "velocity" in $\mathcal{S}^2$. Indeed, if $u_i^{*\alpha}$ denotes the instantaneous velocity of a point in $\mathcal{S}^2$ whose spin is momentarily given by $\sigma_i^{*\alpha}$, then one can write

$$\sigma_i^{*\alpha} = \mathsf{I}_{ij}^{*\alpha} s_j^{*\alpha}\ , \qquad u_i^{*\alpha} = \epsilon_{ijk} s_j^{*\alpha} n_k\ , \qquad \text{with} \qquad \mathsf{I}_{ij}^{*\alpha} = \mathsf{I}_{ji}^{*\alpha}\ , \tag{6.22}$$

where $\mathsf{I}_{ij}^{*\alpha}$ is the specific inertia tensor of constituent α in the orientation n_i. It must be emphasized that the relations (6.22) are in fact *definitions*, which must hold on all levels of description, i.e.

$$\overset{\cdots}{\sigma_i} = \overset{\cdots}{\mathsf{I}_{ij}}\overset{\cdots}{s_j}\ , \qquad \overset{\cdots}{u_i} = \epsilon_{ijk}\overset{\cdots}{s_j}\, n_k\ , \qquad \text{with} \qquad \overset{\cdots}{\mathsf{I}_{ij}} = \overset{\cdots}{\mathsf{I}_{ji}}\ . \tag{6.23}$$

The fields appearing in (6.22) and (6.23) are related by (cf. $(3.61)_{1,2}$)

$$\sigma_i^{\alpha} = \frac{1}{\varrho^{\alpha}}\oint\limits_{\mathcal{S}^2} \varrho^{*\alpha}\sigma_i^{*\alpha}\,\mathrm{d}^2 n\ , \qquad \sigma_i^{*} = \frac{1}{\varrho^{*}}\sum_{\alpha=1}^{N} \varrho^{*\alpha}\sigma_i^{*\alpha}\ , \qquad \sigma_i = \frac{1}{\varrho}\sum_{\alpha=1}^{N}\oint\limits_{\mathcal{S}^2} \varrho^{*\alpha}\sigma_i^{*\alpha}\,\mathrm{d}^2 n\ , \tag{6.24}$$

$$\mathsf{I}_{ij}^{\alpha} = \frac{1}{\varrho^{\alpha}}\oint\limits_{\mathcal{S}^2} \varrho^{*\alpha}\mathsf{I}_{ij}^{*\alpha}\,\mathrm{d}^2 n\ , \qquad \mathsf{I}_{ij}^{*} = \frac{1}{\varrho^{*}}\sum_{\alpha=1}^{N} \varrho^{*\alpha}\mathsf{I}_{ij}^{*\alpha}\ , \qquad \mathsf{I}_{ij} = \frac{1}{\varrho}\sum_{\alpha=1}^{N}\oint\limits_{\mathcal{S}^2} \varrho^{*\alpha}\mathsf{I}_{ij}^{*\alpha}\,\mathrm{d}^2 n\ , \tag{6.25}$$

in such a way that $u_i^{\cdots}$ is usually computed in three steps: ① determination of $\sigma_i^{\cdots}$ and $\mathsf{I}_{ij}^{\cdots}$, ② derivation of $s_i^{\cdots}$ via $(6.23)_1$, ③ calculation of $u_i^{\cdots}$ through $(6.23)_2$. In a similar way as in (6.5), five distinct relative transition rates can be defined:

$$\begin{gathered} U_{\overline{i}}^{*\alpha} = u_i^{*\alpha} - u_i^{*}, \qquad U_i^{*\underline{\alpha}} = u_i^{*\alpha} - u_i^{\alpha}, \qquad U_i^{*\alpha} = u_i^{*\alpha} - u_i, \\ U_i^{*} = u_i^{*} - u_i, \qquad U_i^{\alpha} = u_i^{\alpha} - u_i. \end{gathered} \tag{6.26}$$

It should be noticed, however, that there is in general no counterpart of (6.6) and (6.7) for $U_i^{\cdots}$. This peculiarity gives rise to some interesting issues, as will be shown later on.

The results above provide the necessary background for studying orientational fluxes in $\mathcal{S}^2$. Indeed, let $\mathcal{C}$ denote a (piecewise) smooth oriented curve in a region $\mathcal{P} \subset \mathcal{S}^2$. Its propagation within $\mathcal{P}$ is dictated by the transition rate $u_i^{*c}(x_j, t, n_k)$. Following the same arguments as in Sect. 3.2, one concludes that the constituent orientational flux of an arbitrary additive quantity A across the curve $\mathcal{C}$ is given by

$$\mathsf{G}^{\alpha}(x_i, t, \mathcal{C}) = \int\limits_{\mathcal{C}} (\mathsf{h}_i^{*\alpha} + \mathsf{g}_i^{*\alpha})\, \mathrm{e}_i^{*c}\,\mathrm{d}n, \qquad \mathsf{g}_i^{*\alpha} = \varrho^{*\alpha}\mathsf{a}^{*\alpha}\,(u_i^{*\alpha} - u_i^{*c})\,, \tag{6.27}$$

where e_i^{*c} denotes the unit vector normal to $\mathcal{C}$ (and tangential to the spherical surface of $\mathcal{S}^2$), $\varrho^{*\alpha}\mathsf{a}^{*\alpha}$ is the density of the quantity $\mathsf{A}^{*\alpha}$ and $\mathsf{h}_i^{*\alpha}$ is its transmissive flux density (i.e., its orientational conductive flux density in the space $\mathcal{S}^2$).

Again, there follow from $(6.27)_2$ two situations of special interest:

c) $u_i^{*\mathcal{C}} = 0$ the curve is immobile in $\mathcal{S}^2$ and the flux in $(6.27)_2$ is called (orientationally) *convective*.

d) $u_i^{*\mathcal{W}} = u_i^*$ the curve accompanies the local microstructure motion in $\mathcal{S}^2$, and it is therefore called a *microstructural curve*. Equation $(6.27)_2$ depends in this case on the relative transition rate $U_{\bar{i}}^{*\alpha}$ and the flux is called (orientationally) *diffusive*.

In particular, if one considers the Situation (d) with $U_{\bar{i}}^{*\alpha} = 0$, it follows that $\mathsf{g}_i^* = 0$ and the curve is said to be (orientationally) *impermeable*. Furthermore, by setting $\mathsf{a}^{*\alpha} = 1$ and $\mathsf{h}_i^{*\alpha} = 0$ in (6.27), an expression for the orientational mass flux across the curve $\mathcal{C}$ can be obtained.

As before, the analysis of diffusive fluxes is conspicuously interesting at this stage. By regarding $\mathcal{C}$ as a microstructural curve, (6.27) can be rewritten as

$$\mathsf{G}^{\alpha}(x_i, t, \mathcal{C}) = \int_{\mathcal{C}} (\mathsf{h}_i^{*\alpha} + \varrho^{*\alpha}\mathsf{a}^{*\alpha} U_{\bar{i}}^{*\alpha})\, \mathrm{e}_i^{*c}\, \mathrm{d}n \,, \tag{6.28}$$

in which the transmissive and orientationally diffusive fluxes, viz. $\mathsf{h}_i^{*\alpha}$ and $\varrho^{*\alpha}\mathsf{a}^{*\alpha}U_{\bar{i}}^{*\alpha}$, are easily recognizable. Following the same arguments leading to (3.9), (6.10) and (6.11), summation of (6.28) over all constituents yields

$$\begin{aligned} \mathsf{G}(x_i, t, \mathcal{C}) \;=\; \sum_{\alpha=1}^{N} \mathsf{G}^{\alpha} \;&=\; \sum_{\alpha=1}^{N} \int_{\mathcal{C}} (\mathsf{h}_i^{*\alpha} + \varrho^{*\alpha}\mathsf{a}^{*\alpha} U_{\bar{i}}^{*\alpha})\, \mathrm{e}_i^{*c}\, \mathrm{d}n \\ &= \int_{\mathcal{C}} \sum_{\alpha=1}^{N} (\mathsf{h}_i^{*\alpha} + \varrho^{*\alpha}\mathsf{D}^{*\alpha} U_{\bar{i}}^{*\alpha} + \varrho^{*\alpha}\mathsf{a}^{*} U_{\bar{i}}^{*\alpha})\, \mathrm{e}_i^{*c}\, \mathrm{d}n \\ &= \int_{\mathcal{C}} (\mathsf{h}_i^{*} + \varrho^{*}\mathsf{a}^{*}\Delta_i^{*})\, \mathrm{e}_i^{*c}\, \mathrm{d}n \,, \end{aligned} \tag{6.29}$$

with

$$\mathsf{h}_i^{*} = \sum_{\alpha=1}^{N} (\mathsf{h}_i^{*\alpha} + \varrho^{*\alpha}\mathsf{D}^{*\alpha} U_{\bar{i}}^{*\alpha}) \,, \qquad \varrho^{*}\Delta_i^{*} = \sum_{\alpha=1}^{N} \varrho^{*\alpha} U_{\bar{i}}^{*\alpha} \,. \tag{6.30}$$

The striking feature of (6.29) is that it is not simply a transmissive flux, as one could expect. There is an additional term, $\varrho^{*}\Delta_i^{*}$, which corresponds to a *net diffusive flux of mass in the orientation space*, so that it cannot be included in the definition of transmissive flux density $(6.30)_1$. Such an orientational net flux of mass is a consequence of the simple fact that there exists no counterpart of (6.6) and (6.7) for $U_i^{\cdots}$. The consequences of these results are discussed in Sect. 6.5.

Finally, it can be shown that the completeness assumption, Theorem 5.2.1 (see also (5.21)), is expressed in the orientation space by

$$\oint_{\mathcal{S}^2} \partial_i \mathsf{Q}_i^{*}\, \mathrm{d}^2 n = 0 \,, \tag{6.31}$$

for any continuously differentiable field Q_i^* on $\mathcal{S}^2$, such that $\mathsf{Q}_i^* n_i = 0$. The symbol ∂_i denotes the Cartesian components of the gradient operator in $\mathcal{S}^2$, viz.

$$\partial_i \mathsf{Q}^* = \frac{\partial \mathsf{Q}^*}{\partial n_i} - n_i n_j \frac{\partial \mathsf{Q}^*}{\partial n_j} \,, \tag{6.32}$$

which is called the *orientational gradient* (or orientational divergence, depending on the situation). Actually, (6.31) is a particularization of the following general theorem,

Theorem 6.3.1 (Specialized Green–Stokes). *For any arbitrary continuously differentiable field* $\mathsf{Q}^{\cdots}$ *on* $\mathbb{R}^3$ *there holds*

$$\oint_{\mathcal{S}^2} (\partial_i \mathsf{Q}^{\cdots} - 2 n_i \mathsf{Q}^{\cdots}) \, \mathrm{d}^2 n = 0 \,. \tag{6.33}$$

The proof of (6.33) is given in App. D. In particular, for smooth fields on $\mathcal{S}^2$, (6.33) reduces to (6.31).

It should be noticed that $\mathsf{h}_i^{*\alpha} n_i = 0$ by definition, since transmissive fluxes shall describe conduction phenomena on the orientation space $\mathcal{S}^2$. Consequently,

$$\oint_{\mathcal{S}^2} \partial_i \mathsf{h}_i^{*\alpha} \, \mathrm{d}^2 n = 0 \,. \tag{6.34}$$

Up to now, it has been assumed that all fields are continuous across the surface $\mathcal{W}$. Notwithstanding, most natural surfaces generate field disturbances, often in the form of jump discontinuities, being for this reason called *singular surfaces*. As discussed in Sect. 6.4, fluxes across these surfaces can be treated in the same manner as in regular regions, except by the fact that they may be discontinuous across the surface. Additionally, since one cannot exclude the possibility that such a discontinuity might be produced by the surface itself, a complete theory should take into account the occurrence of surface productions and supplies. These should balance the jumps in fluxes. Effectively,(cf. (3.21))

$$[\![\mathsf{F}^{*\alpha}]\!] = \int_{\mathcal{W}} [\![\mathsf{q}_i^{*\alpha} + \varrho^{*\alpha} \mathsf{a}^{*\alpha} (v_i^{*\alpha} - v_i^{\mathcal{W}})]\!] e_i^{\mathcal{W}} \, \mathrm{d}^2 x = \int_{\mathcal{W}} (\mathsf{b}^{*\alpha} + \mathsf{z}^{*\alpha}) \, \mathrm{d}^2 x, \tag{6.35}$$

where the surface densities of balance $\mathsf{b}^{*\alpha}$ and of external supply $\mathsf{z}^{*\alpha}$ are both defined as smooth functions on $\mathcal{W}$. Finally, from the assumed smoothness of the integrands appearing in (6.35), it can be concluded that, at each point of the singular surface, the *master jump conditions*

$$[\![\mathsf{q}_i^{*\alpha} + \varrho^{*\alpha} \mathsf{a}^{*\alpha} (v_i^{*\alpha} - v_i^{\mathcal{W}})]\!] e_i^{\mathcal{W}} = \mathsf{b}^{*\alpha} + \mathsf{z}^{*\alpha} \tag{6.36}$$

must hold. Furthermore, (3.22) can be recovered by integration of (6.36) over the whole orientation space, with the aid of (6.14) or (6.15) and $(6.16)_2$, provided that

$$\mathsf{b}^{\alpha} + \mathsf{z}^{\alpha} = \oint_{\mathcal{S}^2} (\mathsf{b}^{*\alpha} + \mathsf{z}^{*\alpha}) \, \mathrm{d}^2 n \,. \tag{6.37}$$

6.4 Global and local master balance equations

Let $\mathcal{V}$ represent now a fixed region of $\mathbb{R}^3$ with piecewise smooth boundary $\partial\mathcal{V}$, and assume also that, for the time interval of interest, $\mathcal{V} \subseteq \mathcal{B}$. Similarly, consider simultaneously a fixed region $\mathcal{P}$ of $\mathcal{S}^2$, with piecewise smooth boundary $\partial\mathcal{P}$. As far as the volume $\mathcal{V}$ is fixed in $\mathbb{R}^3$, one has that its boundary is at rest and mass fluxes across $\partial\mathcal{V}$ are convective (Situation (a), Sect. 3.2). Likewise, one concludes that mass fluxes across $\partial\mathcal{P}$ are orientationally convective (Situation (c), Sect. 3.2).

If there are no singularities in $\mathcal{V}$ and $\mathcal{P}$, all points within the product region $\mathcal{V} \times \mathcal{P}$ are called regular, and the standard axiom of balance for a regular region applies, asserting that the time rate of an arbitrary additive property in $\mathcal{V} \times \mathcal{P}$ is balanced by its production inside the region and supplies from outside [290, 317]. Moreover, depending on their causes, such supplies can be classified as fluxes from the neighborhood across the boundaries of $\mathcal{V} \times \mathcal{P}$, or volume interactions with external sources (e.g., due to gravitational and electromagnetic fields). Thence, from the arguments above and the results of Sect. 3.2, one can write for every constituent α of a mixture of microstructured media the following *global master balance equation* (*for regions without singularities*)

$$\int\limits_{\mathcal{V}\times\mathcal{P}} \frac{\partial \varrho^{*\alpha}\mathsf{a}^{*\alpha}}{\partial t}\,\mathrm{d}^2n\,\mathrm{d}^3x \;=\int\limits_{\mathcal{V}\times\mathcal{P}} \varrho^{*\alpha}\mathsf{p}^{*\alpha}\,\mathrm{d}^2n\,\mathrm{d}^3x \;-\int\limits_{\partial\mathcal{V}\times\mathcal{P}} (\mathsf{q}_i^{*\alpha}+\varrho^{*\alpha}\mathsf{a}^{*\alpha}v_i^{*\alpha})\,e_i^{\mathcal{V}}\,\mathrm{d}^2n\,\mathrm{d}^2x$$
$$-\int\limits_{\mathcal{V}\times\partial\mathcal{P}} (\mathsf{h}_i^{*\alpha}+\varrho^{*\alpha}\mathsf{a}^{*\alpha}u_i^{*\alpha})\,e_i^{*\mathcal{P}}\,\mathrm{d}n\,\mathrm{d}^3x \;+\int\limits_{\mathcal{V}\times\mathcal{P}} \varrho^{*\alpha}\mathsf{s}^{*\alpha}\,\mathrm{d}^2n\,\mathrm{d}^3x, \tag{6.38}$$

where use was made of the fact that $\mathcal{V} \times \mathcal{P}$ is fixed in $\mathbb{R}^5$ and free of singularities, which implies the identity

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathsf{A}^{\alpha}(t) \;=\; \frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\mathcal{V}\times\mathcal{P}} \varrho^{*\alpha}\mathsf{a}^{*\alpha}\,\mathrm{d}^2n\,\mathrm{d}^3x \;=\int\limits_{\mathcal{V}\times\mathcal{P}} \frac{\partial}{\partial t}\,(\varrho^{*\alpha}\mathsf{a}^{*\alpha})\;\mathrm{d}^2n\,\mathrm{d}^3x. \tag{6.39}$$

In (6.38) and (6.39), $\varrho^{*\alpha}\mathsf{a}^{*\alpha}$ is the orientation dependent density field of A^{α} and the specific quantities $\mathsf{p}^{*\alpha}$ and $\mathsf{s}^{*\alpha}$ denote its production and external supply, respectively, while $\mathsf{q}_i^{*\alpha}$ and $\mathsf{h}_i^{*\alpha}$ are its conductive fluxes. Moreover, $e_i^{\mathcal{V}}$ and $e_i^{*\mathcal{P}}$ (with $e_i^{*\mathcal{P}} n_i = 0$) denote the unit vectors normal to $\partial\mathcal{V}$ and $\partial\mathcal{P}$, respectively. Notice that fluxes across the edges and corners defined by $\partial\mathcal{V} \times \partial\mathcal{P}$ do not contribute to the balance equation (6.38), since their integrals are assumed to have measure zero.

Finally, from the theorems of Gauss and Stokes [1],

$$\int\limits_{\partial\mathcal{V}\times\mathcal{P}} (\mathsf{q}_i^{*\alpha}+\varrho^{*\alpha}\mathsf{a}^{*\alpha}v_i^{*\alpha})\,e_i^{\mathcal{V}}\,\mathrm{d}^2n\,\mathrm{d}^2x \;=\int\limits_{\mathcal{V}\times\mathcal{P}} \frac{\partial}{\partial x_i}\,(\mathsf{q}_i^{*\alpha}+\varrho^{*\alpha}\mathsf{a}^{*\alpha}v_i^{*\alpha})\,\mathrm{d}^2n\,\mathrm{d}^3x, \tag{6.40}$$

$$\int\limits_{\mathcal{V}\times\partial\mathcal{P}} (\mathsf{h}_i^{*\alpha}+\varrho^{*\alpha}\mathsf{a}^{*\alpha}u_i^{*\alpha})\,e_i^{*\mathcal{P}}\,\mathrm{d}n\,\mathrm{d}^3x \;=\int\limits_{\mathcal{V}\times\mathcal{P}} \partial_i\,(\mathsf{h}_i^{*\alpha}+\varrho^{*\alpha}\mathsf{a}^{*\alpha}u_i^{*\alpha})\,\mathrm{d}^2n\,\mathrm{d}^3x, \tag{6.41}$$

and thence, since the region $\mathcal{V} \times \mathcal{P}$ is arbitrary and the integrands are smooth, one derives from (6.38)–(6.41) the *local master balance equation*

$$\frac{\partial \varrho^{*\alpha} \mathsf{a}^{*\alpha}}{\partial t} + \frac{\partial}{\partial x_i} \left(\varrho^{*\alpha} \mathsf{a}^{*\alpha} v_i^{*\alpha} + \mathsf{q}_i^{*\alpha} \right) + \partial_i \left(\varrho^{*\alpha} \mathsf{a}^{*\alpha} u_i^{*\alpha} + \mathsf{h}_i^{*\alpha} \right) = \varrho^{*\alpha} \mathsf{p}^{*\alpha} + \varrho^{*\alpha} \mathsf{s}^{*\alpha}. \quad (6.42)$$

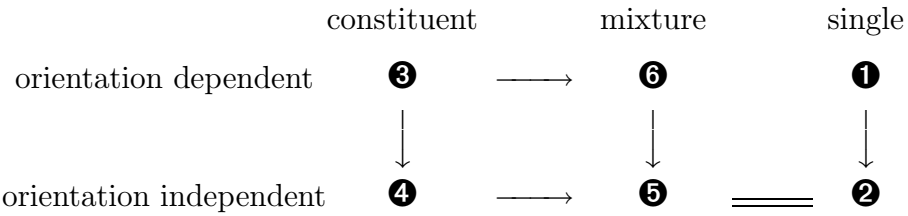
For completeness, the *global master balance equation for a region enclosing a moving singular surface* is also written down, viz.

$$\begin{aligned} &\int_{\mathcal{V}\times\mathcal{P}} \frac{\partial \varrho^{*\alpha} \mathsf{a}^{*\alpha}}{\partial t} \, \mathrm{d}^2 n \, \mathrm{d}^3 x \; - \int_{\mathcal{W}\times\mathcal{P}} [\![\, \varrho^{*\alpha} \mathsf{a}^{*\alpha} \,]\!] v_i^{\mathcal{W}} \mathrm{e}_i^{\mathcal{W}} \mathrm{d}^2 n \, \mathrm{d}^2 x \\ &= \int_{\mathcal{V}\times\mathcal{P}} (\varrho^{*\alpha} \mathsf{p}^{*\alpha} + \varrho^{*\alpha} \mathsf{s}^{*\alpha}) \, \mathrm{d}^2 n \, \mathrm{d}^3 x \; - \int_{\partial\mathcal{V}\times\mathcal{P}} (\mathsf{q}_i^{*\alpha} + \varrho^{*\alpha} \mathsf{a}^{*\alpha} v_i^{*\alpha}) \, \mathrm{e}_i^{\mathcal{V}} \, \mathrm{d}^2 n \, \mathrm{d}^2 x \\ &\quad - \int_{\mathcal{V}\times\partial\mathcal{P}} (\mathsf{h}_i^{*\alpha} + \varrho^{*\alpha} \mathsf{a}^{*\alpha} u_i^{*\alpha}) \, \mathrm{e}_i^{*\mathcal{P}} \, \mathrm{d}n \, \mathrm{d}^3 x \; + \int_{\mathcal{W}\times\mathcal{P}} (\mathsf{b}^{*\alpha} + \mathsf{z}^{*\alpha}) \, \mathrm{d}^2 n \, \mathrm{d}^2 x. \end{aligned} \quad (6.43)$$

The last integral in (6.43) introduces two obvious accretions to (6.38) due to the intrinsic properties of the singular surface $\mathcal{W}$ (cf. Sect. 3.3). They represent additional production and external supply terms, respectively. The second integral on the left-hand side of (6.43) is the appropriate correction of (6.39) when the region $\mathcal{V} \times \mathcal{P}$ is swept by a moving singular surface. Roughly speaking, it is generated by the progressive swallowing of the frontal region $\mathcal{V}^+$ by the singular surface, which extracts an amount $[\![\, \varrho^{*\alpha} \mathsf{a}^{*\alpha} \,]\!]$ from the respective field, releasing the rest in the rear region $\mathcal{V}^-$. In other words, the time rate of the quantity A^α depends, in this case, also on the product of its jump across $\mathcal{W}$ with the volume swept by the singular surface per unit time. Of course, it is easy to infer from standard arguments [221, 290, 317] that (6.43) includes (6.36), (6.38) and (6.42) as particular cases.

6.5 Balance equations for single and mixed media

As observed in Sect. 6.2, the thermodynamics of a mixture of N microstructured media might be described by $8N$ orientation dependent fields, listed in (6.1). As usual, the equations which determine these fields arise from the balance equations of mass, linear and angular momenta and energy, combined with an appropriate set of constitutive relations. On the other hand, the establishment of such constitutive relations requires the introduction of an additional balance equation for the entropy (which is itself a constitutive quantity), completing so the set of nine fundamental balance equations of continuum thermodynamics. Such balance equations will be derived now for single and mixed media, as described in the following scheme:



with

❶ orientation dependent equations for single medium,
❷ equations for single medium,
❸ orientation dependent equations for the α-th constituent,
❹ equations for the α-th constituent,
❺ equations for the mixture,
❻ orientation dependent equations for the mixture,

where

☞ numbers correspond to the order in which the different levels of description are addressed in the text,
☞ arrows indicate the relationship between different description levels,
☞ the = sign designates equivalence of the equations for the two descriptions.

Before presenting the balance equations, it is useful to introduce some common definitions and remarks. First, the adjective *orientational* is attributed to certain fields in order to emphasize that they represent properties on $\mathcal{S}^2$. Hence, if a^*_i and b^*_{ij} are,respectively, orientational vector and tensor valued fields, then

$$\mathsf{a}^*_i n_i = \mathsf{b}^*_{ij} n_j = 0 \,. \tag{6.44}$$

Second, associated to the total energy and angular momentum of a given medium, the following specific quantities are defined

$$L_i^{\cdots} = \epsilon_{ijk} x_j v_k^{\cdots} + \sigma_i^{\cdots}\,, \qquad K_i^{\cdots} = \epsilon_{ijk} x_j g_k^{\cdots} + c_i^{\cdots}\,, \qquad N_i^{\cdots} = \epsilon_{ijk} x_j \kappa_k^{\cdots} + \nu_i^{\cdots}\,, \tag{6.45}$$

$$E^{\cdots} = e^{\cdots} + \frac{v_i^{\cdots} v_i^{\cdots}}{2} + \frac{\sigma_i^{\cdots} s_i^{\cdots}}{2}, \quad R^{\cdots} = r^{\cdots} + g_i^{\cdots} v_i^{\cdots} + c_i^{\cdots} s_i^{\cdots}\,, \quad P^{\cdots} = \varepsilon^{\cdots} + \kappa_i^{\cdots} v_i^{\cdots} + \nu_i^{\cdots} s_i^{\cdots}\,, \tag{6.46}$$

as well as the fluxes

$$\mathsf{M}_{il}^{\cdots} = \epsilon_{ijk} x_j \mathsf{t}_{kl}^{\cdots} + \mathsf{m}_{il}^{\cdots}\,, \qquad \mathsf{X}_{il}^{\cdots} = \epsilon_{ijk} x_j \boldsymbol{\tau}_{kl}^{\cdots} + \boldsymbol{\varpi}_{il}^{\cdots}\,, \tag{6.47}$$

$$Q_j^{\cdots} = q_j^{\cdots} - \mathsf{t}_{ij}^{\cdots} v_i^{\cdots} - \mathsf{m}_{ij}^{\cdots} s_i^{\cdots}\,, \qquad \Xi_j^{\cdots} = \xi_j^{\cdots} - \boldsymbol{\tau}_{ij}^{\cdots} v_i^{\cdots} - \boldsymbol{\varpi}_{ij}^{\cdots} s_i^{\cdots}\,, \tag{6.48}$$

where

$c_i^{\cdots}$ ... specific external couple;
$e^{\cdots}$ ... specific internal energy;
$E^{\cdots}$ .. specific total energy;
$g_i^{\cdots}$ ... specific external force;
$K_i^{\cdots}$ .. specific total external couple;
$L_i^{\cdots}$ ... specific total angular momentum;
$\mathsf{m}_{ij}^{\cdots}$ .. Voigt couple stress;
$\mathsf{M}_{ij}^{\cdots}$ .. total couple of stresses;

$N_i^{\cdots}$ .. specific total interaction couple;

$P^{\cdots}$ .. specific production rate of total energy;

$q_i^{\cdots}$ ... heat flux density;

$Q_i^{\cdots}$ .. total energy flux density;

$r^{\cdots}$ ... specific external supply of internal energy;

$R^{\cdots}$ .. specific external supply of total energy;

$s_i^{\cdots}$ ... spin velocity;

$v_i^{\cdots}$ ... translational velocity;

$\varepsilon^{\cdots}$ ... specific production rate of internal energy;

$\kappa_i^{\cdots}$ ... specific interaction force;

$\nu_i^{\cdots}$ ... specific interaction couple;

$\xi_i^{\cdots}$ ... orientational heat flux density;

$\Xi_i^{\cdots}$ .. orientational flux density of total energy;

$\boldsymbol{\varpi}_{ij}^{\cdots}$ .. orientational couple stress;

$\mathsf{X}_{ij}^{\cdots}$ ... orientational total couple of stresses;

$\sigma_i^{\cdots}$ ... specific spin;

$\boldsymbol{\tau}_{ij}^{\cdots}$ ... orientational stress.

$\phi_i^{\cdots}$ ... entropy flux density;

$\varphi_i^{\cdots}$ ... orientational entropy flux density.

The orientational fluxes listed above obey the conditions[2] (cf. (6.44))

$$\boldsymbol{\tau}_{ij}^{\cdots} n_j = \boldsymbol{\varpi}_{ij}^{\cdots} n_j = \xi_i^{\cdots} n_i = \varphi_i^{\cdots} n_i = 0 \,, \tag{6.49}$$

in such a way that, from (6.33),

$$\oint_{\mathcal{S}^2} \partial_j \boldsymbol{\tau}_{ij}^{\cdots} \, \mathrm{d}^2 n \;=\; \oint_{\mathcal{S}^2} \partial_j \boldsymbol{\varpi}_{ij}^{\cdots} \, \mathrm{d}^2 n \;=\; \oint_{\mathcal{S}^2} \partial_i \xi_i^{\cdots} \, \mathrm{d}^2 n \;=\; \oint_{\mathcal{S}^2} \partial_i \varphi_i^{\cdots} \, \mathrm{d}^2 n \;=\; 0 \,. \tag{6.50}$$

At last, it must be stressed that the relations below are generally valid with respect to *inertial frames of reference*. Eventual complications arising from inertial effects are not regarded at this stage.

❶ *Orientation dependent equations for single medium*

For a single medium with microstructure, the following orientation dependent balance equations of mass, linear and angular momenta, energy and entropy can be derived[3] from (6.42)

[2]Notice that the transition rate u_i^* is also an orientational field and, by definition (see (6.23)), $u_i^* n_i = 0$. In contrast, the spin velocity s_i^* is not an orientational field because it describes rotations in the three-dimensional space. In fact, it must be kept in mind that each primitive element of the microstructure has indeed three rotational degrees of freedom (which can be related to changes of its three Euler angles) implying that $s_i^{\cdots} n_i \neq 0$ generally holds [88], a fact which has been recognized even for crystalline media [166], suspensions [56, 129] and liquid crystals [270]. On the other hand, as far as every microstructural element is assumed to manifest an axially symmetric behavior, implying isotropy in planes orthogonal to its symmetry axis, there follows that the value of its third Euler angle (which measures rotations of the element about its symmetry axis) is redundant, even though its time rate is not. Consequently, only two angles suffice to characterize the microstructural elements of each constituent at any instant and position, in such a way that primitive microstructural elements of the same constituent whose symmetry axes are parallel cannot be distinguished, being characterized by a single point on $\mathcal{S}^2$.

[3]It should be noticed that internal production of mass must be accounted for in (6.51) as to describe some outstanding phenomena, like e.g. recrystallization in a polycrystalline material.

$$\frac{\partial \varrho^*}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^* v_i^*\right) + \partial_i\left(\varrho^* u_i^*\right) = \varrho^* \Gamma^*, \tag{6.51}$$

$$\frac{\partial \varrho^* v_i^*}{\partial t} + \frac{\partial}{\partial x_j}\left(\varrho^* v_i^* v_j^* - \mathsf{t}_{ij}^*\right) + \partial_j\left(\varrho^* v_i^* u_j^* - \boldsymbol{\tau}_{ij}^*\right) = \varrho^* \kappa_i^* + \varrho^* g_i^*, \tag{6.52}$$

$$\frac{\partial \varrho^* L_i^*}{\partial t} + \frac{\partial}{\partial x_j}\left(\varrho^* L_i^* v_j^* - \mathsf{M}_{ij}^*\right) + \partial_j\left(\varrho^* L_i^* u_j^* - \mathsf{X}_{ij}^*\right) = \varrho^* N_i^* + \varrho^* K_i^*, \tag{6.53}$$

$$\frac{\partial \varrho^* E^*}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^* E^* v_i^* + Q_i^*\right) + \partial_i\left(\varrho^* E^* u_i^* + \Xi_i^*\right) = \varrho^* P^* + \varrho^* R^*, \tag{6.54}$$

$$\frac{\partial \varrho^* \eta^*}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^* \eta^* v_i^* + \phi_i^*\right) + \partial_i\left(\varrho^* \eta^* u_i^* + \varphi_i^*\right) = \varrho^* \varsigma^* + \varrho^* s^*, \tag{6.55}$$

where (6.53) can be rewritten with the help of (6.45)-(6.48) and (6.52) as

$$\frac{\partial \varrho^* \sigma_i^*}{\partial t} + \frac{\partial}{\partial x_j}\left(\varrho^* \sigma_i^* v_j^* - \mathsf{m}_{ij}^*\right) + \partial_j\left(\varrho^* \sigma_i^* u_j^* - \boldsymbol{\varpi}_{ij}^*\right) + \epsilon_{ijk} t_{jk}^* = \varrho^* \nu_i^* + \varrho^* c_i^*\,, \tag{6.56}$$

which expresses the orientation dependent balance equation of spin.

❷ *Equations for single medium*

From the results established up to now, and in particular from those presented in Sects. 6.3 and 6.2, one can propose the following definitions for the density fields of the medium[4] (valid for inertial observers)

$$\mathsf{Y} = \oint_{\mathcal{S}^2} \mathsf{Y}^*\, \mathrm{d}^2 n, \qquad\qquad \oint_{\mathcal{S}^2} \mathsf{Z}^*\, \mathrm{d}^2 n = 0, \tag{6.57}$$

$$\mathsf{Y} = \{\, \varrho\,,\ \varrho v_i\,,\ \varrho L_i\,,\ \varrho E\,,\ \varrho\eta\ ;\ \varrho g_i\,,\ \varrho K_i\,,\ \varrho R\,,\ \varrho s\ ;\ \varrho\varsigma\,\}\,,$$
$$\mathsf{Z} = \{\, \varrho\Gamma\,,\ \varrho\kappa_i\,,\ \varrho N_i\,,\ \varrho P\,\}\,,$$

as well as for their fluxes

$$\mathsf{t}_{ij} = \oint_{\mathcal{S}^2} \left(\mathsf{t}_{ij}^* - \varrho^* C_i^* C_j^*\right) \mathrm{d}^2 n, \qquad Q_i = \oint_{\mathcal{S}^2} \left(Q_i^* + \varrho^* V^* C_i^*\right) \mathrm{d}^2 n, \tag{6.58}$$

$$\mathsf{M}_{ij} = \oint_{\mathcal{S}^2} \left(\mathsf{M}_{ij}^* - \varrho^* Z_i^* C_j^*\right) \mathrm{d}^2 n, \qquad \phi_i = \oint_{\mathcal{S}^2} \left(\phi_i^* + \varrho^* H^* C_i^*\right) \mathrm{d}^2 n. \tag{6.59}$$

Eqs. $(6.57)_1$ simply reflect the additivity of the densities involved (cf. (5.3) and $(5.9)_1$), whereas the vanishing integrals in $(6.57)_2$ are consequences of the conservation of mass, momenta and energy. On the other hand, the conductive fluxes defined

[4]The abbreviations introduced in (6.57) will be frequently employed from now on, and they imply that

$$\varrho = \oint_{\mathcal{S}^2} \varrho^*\, \mathrm{d}^2 n, \qquad \varrho L_i = \oint_{\mathcal{S}^2} \varrho^* L_i^*\, \mathrm{d}^2 n, \qquad \oint_{\mathcal{S}^2} \varrho^* \Gamma^*\, \mathrm{d}^2 n = 0, \qquad \text{etc.}$$

in (6.58) and (6.59) arise from diffusive as well as conductive fluxes, in accordance with the general definition (6.19).

Hence, from (6.50) and (6.51)–(6.59) the usual *balance equations for polar media* are obtained

$$\frac{\partial \varrho}{\partial t} + \frac{\partial}{\partial x_i}(\varrho v_i) = 0, \tag{6.60}$$

$$\frac{\partial \varrho v_i}{\partial t} + \frac{\partial}{\partial x_j}(\varrho v_i v_j - \mathsf{t}_{ij}) = \varrho g_i, \tag{6.61}$$

$$\frac{\partial \varrho L_i}{\partial t} + \frac{\partial}{\partial x_j}(\varrho L_i v_j - \mathsf{M}_{ij}) = \varrho K_i, \tag{6.62}$$

$$\frac{\partial \varrho E}{\partial t} + \frac{\partial}{\partial x_i}(\varrho E v_i + Q_i) = \varrho R, \tag{6.63}$$

$$\frac{\partial \varrho \eta}{\partial t} + \frac{\partial}{\partial x_i}(\varrho \eta v_i + \phi_i) = \varrho \varsigma + \varrho s. \tag{6.64}$$

Again, (6.62) can be also simplified to

$$\frac{\partial \varrho \sigma_i}{\partial t} + \frac{\partial}{\partial x_j}(\varrho \sigma_i v_j - \mathsf{m}_{ij}) + \epsilon_{ijk} t_{jk} = \varrho c_i, \tag{6.65}$$

while from (6.45)–(6.48) and (6.51)-(6.59), one finds

$$\varrho\sigma_i = \oint_{\mathcal{S}^2} \varrho^* \sigma_i^* \, \mathrm{d}^2 n \,, \qquad \varrho c_i = \oint_{\mathcal{S}^2} \varrho^* c_i^* \, \mathrm{d}^2 n \,, \qquad \oint_{\mathcal{S}^2} \varrho^* \nu_i^* \, \mathrm{d}^2 n = 0 \,, \tag{6.66}$$

$$\varrho \mathsf{I}_{ij} = \oint_{\mathcal{S}^2} \varrho^* \mathsf{I}_{ij}^* \, \mathrm{d}^2 n \,, \qquad \mathsf{m}_{ij} = \oint_{\mathcal{S}^2} \big(\mathsf{m}_{ij}^* - \varrho^* \Sigma_i^* C_j^*\big) \mathrm{d}^2 n \,, \tag{6.67}$$

$$\varrho e = \oint_{\mathcal{S}^2} \varrho^* \left(e^* + \frac{C_i^* C_i^*}{2} + \mathsf{I}_{ij}^* \frac{S_i^* S_j^*}{2} \right) \mathrm{d}^2 n \,, \tag{6.68}$$

$$\varrho r = \oint_{\mathcal{S}^2} \varrho^* \big(r^* + g_i^* C_i^* + c_i^* S_i^*\big) \mathrm{d}^2 n \,, \qquad \oint_{\mathcal{S}^2} \varrho^* \big(\varepsilon^* + \kappa_i^* C_i^* + \nu_i^* S_i^*\big) \mathrm{d}^2 n = 0 \,, \tag{6.69}$$

$$q_k = \oint_{\mathcal{S}^2} \left[q_k^* - \mathsf{t}_{ik}^* C_i^* - \mathsf{m}_{ik}^* S_i^* + \varrho^* \left(W^* + \frac{C_i^* C_i^*}{2} + \mathsf{I}_{ij}^* \frac{S_i^* S_j^*}{2} \right) C_k^* - \varrho^* \mathsf{J}_{ij}^* \frac{s_i s_j}{2} C_k^* \right] \mathrm{d}^2 n \,. \tag{6.70}$$

Equations (6.51)–(6.70) are compatible with the statistical theory of Dahler [85], although they are not identical to the expressions proposed by Curtiss [84] for rarefied gases nor with those presented later in the phenomenological theory of Condiff & Brenner [78]. The sources of these differences are the low density limit posited by Curtiss and the nowadays less usual definitions for stresses and fluxes employed by

Condiff & Brenner. On the other hand, Blenk et al. [46] neglected interaction terms and used $s_i^* n_i = 0$, which made their expressions more restrictive than (6.66)–(6.70).

As a final remark, although we did not invoke explicitly in this section the metaphysical principles of Truesdell[5] have not been explicitly invoked, as done for instance in [129], it is obvious that they must be fulfilled. Indeed, as far as the balance equations (6.60)–(6.65) are known and well founded in the literature of polar media, these principles reduce to a reasonable, and in fact obvious, requirement of compatibility between the balance equations (6.51)–(6.56) and (6.60)–(6.65). In other words, for microstructured single media modelled as mixtures with continuous diversity, Truesdell's metaphysical principles have nothing of "metaphysical" at all!

❸ *Orientation dependent equations for constituents*

As discussed in Sect. 6.2, usually $8N$ orientation dependent fields are needed to describe the thermodynamics of a mixture of N microstructured media (cf. (6.1)). Moreover, from arguments similar to those presented for a single medium in ❶, it follows that the appropriate field equations for such materials can be derived from $9N$ balance equations of mass, linear and angular momenta, energy and entropy, viz.

$$\frac{\partial \varrho^{*\alpha}}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^{*\alpha} v_i^{*\alpha}\right) + \partial_i\left(\varrho^{*\alpha} u_i^{*\alpha}\right) = \varrho^{*\alpha}\Gamma^{*\alpha}, \tag{6.71}$$

$$\frac{\partial \varrho^{*\alpha} v_i^{*\alpha}}{\partial t} + \frac{\partial}{\partial x_j}\left(\varrho^{*\alpha} v_i^{*\alpha} v_j^{*\alpha} - \mathsf{t}_{ij}^{*\alpha}\right) + \partial_j\left(\varrho^{*\alpha} v_i^{*\alpha} u_j^{*\alpha} - \boldsymbol{\tau}_{ij}^{*\alpha}\right) = \varrho^{*\alpha}\kappa_i^{*\alpha} + \varrho^{*\alpha} g_i^{*\alpha}, \tag{6.72}$$

$$\frac{\partial \varrho^{*\alpha} L_i^{*\alpha}}{\partial t} + \frac{\partial}{\partial x_j}\left(\varrho^{*\alpha} L_i^{*\alpha} v_j^{*\alpha} - \mathsf{M}_{ij}^{*\alpha}\right) + \partial_j\left(\varrho^{*\alpha} L_i^{*\alpha} u_j^{*\alpha} - \mathsf{X}_{ij}^{*\alpha}\right) = \varrho^{*\alpha} N_i^{*\alpha} + \varrho^{*\alpha} K_i^{*\alpha}\,, \tag{6.73}$$

$$\frac{\partial \varrho^{*\alpha} E^{*\alpha}}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^{*\alpha} E^{*\alpha} v_i^{*\alpha} + Q_i^{*\alpha}\right) + \partial_i\left(\varrho^{*\alpha} E^{*\alpha} u_i^{*\alpha} + \Xi_i^{*\alpha}\right) = \varrho^{*\alpha} P^{*\alpha} + \varrho^{*\alpha} R^{*\alpha}\,, \tag{6.74}$$

$$\frac{\partial \varrho^{*\alpha} \eta^{*\alpha}}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^{*\alpha} \eta^{*\alpha} v_i^{*\alpha} + \phi_i^{*\alpha}\right) + \partial_i\left(\varrho^{*\alpha} \eta^{*\alpha} u_i^{*\alpha} + \varphi_i^{*\alpha}\right) = \varrho^{*\alpha}\varsigma^{*\alpha} + \varrho^{*\alpha} s^{*\alpha}, \tag{6.75}$$

which can be obtained from (6.51)–(6.55) after consideration of N microstructured media (i.e., through substitution of the superscripts "$*$" by "$*\alpha$"), or alternatively, through direct derivation from (6.42). As before, (6.73) can be simplified with the aid of (6.45)–(6.48) and (6.72) to

$$\frac{\partial \varrho^{*\alpha} \sigma_i^{*\alpha}}{\partial t} + \frac{\partial}{\partial x_j}\left(\varrho^{*\alpha} \sigma_i^{*\alpha} v_j^{*\alpha} - \mathsf{m}_{ij}^{*\alpha}\right) + \partial_j\left(\varrho^{*\alpha} \sigma_i^{*\alpha} u_j^{*\alpha} - \boldsymbol{\varpi}_{ij}^{*\alpha}\right) + \epsilon_{ijk} t_{jk}^{*\alpha} = \varrho^{*\alpha} \nu_i^{*\alpha} + \varrho^{*\alpha} c_i^{*\alpha}\,. \tag{6.76}$$

[5] Concisely, the *metaphysical principles* of Truesdell [405] state that: 1) all properties of the mixture are mathematical consequences of the constituent properties; 2) so as to describe the motion of a constituent, one can imagine it isolated from the rest of the mixture, provided the actions of the other constituents upon it are allowed; 3) the motion of the mixture is governed by the same equations as a single medium.

The respective expressions for the mixture itself can be determined in two ways, both involving integration over all orientations and sum over all constituents. They differ only by the order in which these two procedures are carried out. Although the final results are obviously the same, since the summation over all α commutes with the integration over the whole $\mathcal{S}^2$, the intermediate results are distinct and reveal some very interesting features which will be addressed now.

❹ *Equations for constituents*

Suppose one chooses to perform first the integration over $\mathcal{S}^2$. In analogy with the case of a single medium ❶, one can propose the following definitions for the density fields of the constituents (cf. (5.3) and $(5.9)_1$),

$$\mathsf{Y}^\alpha = \oint_{\mathcal{S}^2} \mathsf{Y}^{*\alpha}\, \mathrm{d}^2 n, \tag{6.77}$$

$$\mathsf{Y} = \{\, \varrho\,,\ \varrho v_i\,,\ \varrho L_i\,,\ \varrho E\,,\ \varrho\eta\ ;\ \varrho g_i\,,\ \varrho K_i\,,\ \varrho R\,,\ \varrho s\ ;\ \varrho\Gamma\,,\ \varrho\kappa_i\,,\ \varrho N_i\,,\ \varrho P\,,\ \varrho\varsigma\,\}\,,$$

as well as for their fluxes (cf. (6.14))

$$\mathsf{t}^\alpha_{ij} = \oint_{\mathcal{S}^2} \left(\mathsf{t}^{*\alpha}_{ij} - \varrho^{*\alpha} C^{*\underline{\alpha}}_i C^{*\underline{\alpha}}_j\right) \mathrm{d}^2 n, \qquad Q^\alpha_i = \oint_{\mathcal{S}^2} \left(Q^{*\alpha}_i + \varrho^{*\alpha} V^{*\underline{\alpha}} C^{*\underline{\alpha}}_i\right) \mathrm{d}^2 n, \tag{6.78}$$

$$\mathsf{M}^\alpha_{ij} = \oint_{\mathcal{S}^2} \left(\mathsf{M}^{*\alpha}_{ij} - \varrho^{*\alpha} Z^{*\underline{\alpha}}_i C^{*\underline{\alpha}}_j\right) \mathrm{d}^2 n, \qquad \phi^\alpha_i = \oint_{\mathcal{S}^2} \left(\phi^{*\alpha}_i + \varrho^{*\alpha} H^{*\underline{\alpha}} C^{*\underline{\alpha}}_i\right) \mathrm{d}^2 n\,. \tag{6.79}$$

Consequently, from (6.50) and (6.71)–(6.79) one obtains balance equations for the constituents of a chemical mixture with microstructure which are identical to those proposed in Chap. 3, (3.25)–(3.33), viz.

$$\frac{\partial \varrho^\alpha}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^\alpha v^\alpha_i\right) = \varrho^\alpha \Gamma^\alpha\,, \tag{6.80}$$

$$\frac{\partial \varrho^\alpha v^\alpha_i}{\partial t} + \frac{\partial}{\partial x_j}\left(\varrho^\alpha v^\alpha_i v^\alpha_j - \mathsf{t}^\alpha_{ij}\right) = \varrho^\alpha \kappa^\alpha_i + \varrho^\alpha g^\alpha_i\,, \tag{6.81}$$

$$\frac{\partial \varrho^\alpha L^\alpha_i}{\partial t} + \frac{\partial}{\partial x_j}\left(\varrho^* L^\alpha_i v^\alpha_j - \mathsf{M}^\alpha_{ij}\right) = \varrho^\alpha N^\alpha_i + \varrho^\alpha K^\alpha_i\,, \tag{6.82}$$

$$\frac{\partial \varrho^\alpha E^\alpha}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^\alpha E^\alpha v^\alpha_i + Q^\alpha_i\right) = \varrho^\alpha P^\alpha + \varrho^\alpha R^\alpha\,, \tag{6.83}$$

$$\frac{\partial \varrho^\alpha \eta^\alpha}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^\alpha \eta^\alpha v^\alpha_i + \phi^\alpha_i\right) = \varrho^\alpha \varsigma^\alpha + \varrho^\alpha s^\alpha\,, \tag{6.84}$$

and, as before, (6.82) can be simplified to

$$\frac{\partial \varrho^\alpha \sigma^\alpha_i}{\partial t} + \frac{\partial}{\partial x_j}\left(\varrho^\alpha \sigma^\alpha_i v^\alpha_j - \mathsf{m}^\alpha_{ij}\right) + \epsilon_{ijk} t^\alpha_{jk} = \varrho^\alpha \nu^\alpha_i + \varrho^\alpha c^\alpha_i\,, \tag{6.85}$$

while from (6.45)-(6.48) and (6.71)–(6.79) follow

$$\varrho^{\alpha}\sigma_i^{\alpha} = \oint_{\mathcal{S}^2} \varrho^{*\alpha}\sigma_i^{*\alpha}\,\mathrm{d}^2n, \qquad \varrho^{\alpha}c_i^{\alpha} = \oint_{\mathcal{S}^2} \varrho^{*\alpha}c_i^{*\alpha}\,\mathrm{d}^2n, \qquad \varrho^{\alpha}\nu_i^{\alpha} = \oint_{\mathcal{S}^2} \varrho^{*\alpha}\nu_i^{*\alpha}\,\mathrm{d}^2n, \tag{6.86}$$

$$\varrho^{\alpha}\mathsf{I}_{ij}^{\alpha} = \oint_{\mathcal{S}^2} \varrho^{*\alpha}\mathsf{I}_{ij}^{*\alpha}\,\mathrm{d}^2n\,, \qquad \mathsf{m}_{ij}^{\alpha} = \oint_{\mathcal{S}^2} \big(\mathsf{m}_{ij}^{*\alpha} - \varrho^{*\alpha}\Sigma_i^{*\underline{\alpha}}C_j^{*\underline{\alpha}}\big)\mathrm{d}^2n, \tag{6.87}$$

$$\varrho^{\alpha}e^{\alpha} = \oint_{\mathcal{S}^2} \varrho^{*\alpha}\left(e^{*\alpha} + \frac{C_i^{*\underline{\alpha}}C_i^{*\underline{\alpha}}}{2} + \mathsf{I}_{ij}^{*\alpha}\frac{S_i^{*\underline{\alpha}}S_j^{*\underline{\alpha}}}{2}\right)\mathrm{d}^2n\,, \tag{6.88}$$

$$\varrho^{\alpha}r^{\alpha} = \oint_{\mathcal{S}^2} \varrho^{*\alpha}\big(r^{*\alpha} + g_i^{*\alpha}C_i^{*\underline{\alpha}} + c_i^{*\alpha}S_i^{*\underline{\alpha}}\big)\mathrm{d}^2n\,, \tag{6.89}$$

$$\varrho^{\alpha}\varepsilon^{\alpha} = \oint_{\mathcal{S}^2} \varrho^{*\alpha}\big(\varepsilon^{*\alpha} + \kappa_i^{*\alpha}C_i^{*\underline{\alpha}} + \nu_i^{*\alpha}S_i^{*\underline{\alpha}}\big)\mathrm{d}^2n\,, \tag{6.90}$$

$$q_k^{\alpha} = \oint_{\mathcal{S}^2}\Bigg[q_k^{*\alpha} - \mathsf{t}_{ik}^{*\alpha}C_i^{*\underline{\alpha}} - \mathsf{m}_{ik}^{*\alpha}S_i^{*\underline{\alpha}} + \varrho^{*\alpha}\Bigg(W^{*\alpha} + \frac{C_i^{*\underline{\alpha}}C_i^{*\underline{\alpha}}}{2} + \mathsf{I}_{ij}^{*\alpha}\frac{S_i^{*\underline{\alpha}}S_j^{*\underline{\alpha}}}{2}\Bigg)C_k^{*\underline{\alpha}} - \varrho^{*\alpha}\mathsf{J}_{ij}^{*\underline{\alpha}}\frac{s_i^{\alpha}s_j^{\alpha}}{2}C_k^{*\underline{\alpha}}\Bigg]\mathrm{d}^2n\,. \tag{6.91}$$

❺ *Equations for the mixture*

As long as the balance equations (6.80)–(6.82) are the same as those discussed in Chap. 3, it follows that all the expressions relating mixture and constituent fields must be just the ones presented in Sects. 3.4 and 3.5. The analysis does not need to be repeated.

❻ *Orientation dependent equations for the mixture*

Returning to (6.71)-(6.76), suppose that one chooses to perform first the sum of those equations over all constituents. Basing on the experience acquired in the last sections, one can propose the following definitions for the orientation dependent density fields of the mixture (cf. (6.3) and (6.4))

$$\mathsf{Y}^{*} = \sum_{\alpha=1}^{N}\mathsf{Y}^{*\alpha}, \tag{6.92}$$

$$\mathsf{Y} = \{\,\varrho\,,\ \varrho v_i\,,\ \varrho L_i\,,\ \varrho E\,,\ \varrho\eta\ ;\ \varrho g_i\,,\ \varrho K_i\,,\ \varrho R\,,\ \varrho s\ ;\ \varrho\Gamma\,,\ \varrho\kappa_i\,,\ \varrho N_i\,,\ \varrho P\,,\ \varrho\varsigma\,\}\,,$$

as well as for their fluxes (cf. (6.12))

$$\mathsf{t}_{ij}^{*} = \sum_{\alpha=1}^{N}\big(\mathsf{t}_{ij}^{*\alpha} - \varrho^{*\alpha}C_i^{*\underline{\alpha}}C_j^{*\underline{\alpha}}\big)\,, \qquad Q_i^{*} = \sum_{\alpha=1}^{N}\big(Q_i^{*\alpha} + \varrho^{*\alpha}V^{*\underline{\alpha}}C_i^{*\underline{\alpha}}\big)\,, \tag{6.93}$$

$$\mathsf{M}^*_{ij} = \sum_{\alpha=1}^{N} \left(\mathsf{M}^{*\alpha}_{ij} - \varrho^{*\alpha} Z^{*\alpha}_{\underline{i}} C^{*\alpha}_{\underline{j}}\right), \qquad \phi^*_i = \sum_{\alpha=1}^{N} \left(\phi^{*\alpha}_i + \varrho^{*\alpha} H^{*\alpha}_{\underline{-}} C^{*\alpha}_{\underline{i}}\right), \tag{6.94}$$

$$\mathsf{\tau}^*_{ij} = \sum_{\alpha=1}^{N} \left(\mathsf{\tau}^{*\alpha}_{ij} - \varrho^{*\alpha} C^{*\alpha}_{\underline{i}} U^{*\alpha}_{\underline{j}}\right), \qquad \Xi^*_i = \sum_{\alpha=1}^{N} \left(\Xi^{*\alpha}_i + \varrho^{*\alpha} V^{*\alpha}_{\underline{-}} U^{*\alpha}_{\underline{i}}\right), \tag{6.95}$$

$$\mathsf{X}^*_{ij} = \sum_{\alpha=1}^{N} \left(\mathit{\Pi}^{*\alpha}_{ij} - \varrho^{*\alpha} Z^{*\alpha}_{\underline{i}} U^{*\alpha}_{\underline{j}}\right), \qquad \varphi^*_i = \sum_{\alpha=1}^{N} \left(\varphi^{*\alpha}_i + \varrho^{*\alpha} H^{*\alpha}_{\underline{-}} U^{*\alpha}_{\underline{i}}\right). \tag{6.96}$$

Moreover, from (6.45)–(6.48), (6.23), (6.71)-(6.76) and (6.92)–(6.96) follow the relations

$$\varrho^* \sigma^*_i = \sum_{\alpha=1}^{N} \varrho^{*\alpha} \sigma^{*\alpha}_i, \qquad \varrho^* c^*_i = \sum_{\alpha=1}^{N} \varrho^{*\alpha} c^{*\alpha}_i, \qquad \varrho^* \nu^*_i = \sum_{\alpha=1}^{N} \varrho^{*\alpha} \nu^{*\alpha}_i, \tag{6.97}$$

$$\mathsf{m}^*_{ij} = \sum_{\alpha=1}^{N} \big(\mathsf{m}^{*\alpha}_{ij} - \varrho^{*\alpha} \mathit{\Sigma}^{*\alpha}_{\underline{i}} C^{*\alpha}_{\underline{j}}\big), \qquad \mathsf{\varpi}^*_{ij} = \sum_{\alpha=1}^{N} \big(\mathsf{\varpi}^{*\alpha}_{ij} - \varrho^{*\alpha} \mathit{\Sigma}^{*\alpha}_{\underline{i}} U^{*\alpha}_{\underline{j}}\big), \tag{6.98}$$

$$\varrho^* \mathsf{I}^*_{ij} = \sum_{\alpha=1}^{N} \varrho^{*\alpha} \mathsf{I}^{*\alpha}_{ij}, \qquad \varrho^* e^* = \sum_{\alpha=1}^{N} \varrho^{*\alpha} \left(e^{*\alpha} + \frac{C^{*\alpha}_{\underline{i}} C^{*\alpha}_{\underline{i}}}{2} + \mathsf{I}^{*\alpha}_{ij} \frac{S^{*\alpha}_{\underline{i}} S^{*\alpha}_{\underline{j}}}{2}\right), \tag{6.99}$$

$$\varrho^* r^* = \sum_{\alpha=1}^{N} \varrho^{*\alpha} \big(r^{*\alpha} + g^{*\alpha}_i C^{*\alpha}_{\underline{i}} + c^{*\alpha}_i S^{*\alpha}_{\underline{i}}\big), \tag{6.100}$$

$$\varrho^* \varepsilon^* = \sum_{\alpha=1}^{N} \varrho^{*\alpha} \left(\varepsilon^{*\alpha} + \kappa^{*\alpha}_i C^{*\alpha}_{\underline{i}} + \nu^{*\alpha}_i S^{*\alpha}_{\underline{i}}\right), \tag{6.101}$$

$$q^*_k = \sum_{\alpha=1}^{N} \Bigg[q^{*\alpha}_k - \mathsf{t}^{*\alpha}_{ik} C^{*\alpha}_{\underline{i}} - \mathsf{m}^{*\alpha}_{ik} S^{*\alpha}_{\underline{i}} + \varrho^{*\alpha} \Bigg(W^{*\alpha} + \frac{C^{*\alpha}_{\underline{i}} C^{*\alpha}_{\underline{i}}}{2} + \mathsf{I}^{*\alpha}_{ij} \frac{S^{*\alpha}_{\underline{i}} S^{*\alpha}_{\underline{j}}}{2} \Bigg) C^{*\alpha}_{\underline{k}} - \varrho^{*\alpha} \mathsf{J}^{*\alpha}_{\underline{ij}} \frac{s^*_i s^*_j}{2} C^{*\alpha}_{\underline{k}} \Bigg], \tag{6.102}$$

$$\xi^*_k = \sum_{\alpha=1}^{N} \Bigg[\xi^{*\alpha}_k - \mathsf{\tau}^{*\alpha}_{ik} C^{*\alpha}_{\underline{i}} - \mathsf{\varpi}^{*\alpha}_{ik} S^{*\alpha}_{\underline{i}} + \varrho^{*\alpha} \Bigg(W^{*\alpha} + \frac{C^{*\alpha}_{\underline{i}} C^{*\alpha}_{\underline{i}}}{2} + \mathsf{I}^{*\alpha}_{ij} \frac{S^{*\alpha}_{\underline{i}} S^{*\alpha}_{\underline{j}}}{2} \Bigg) U^{*\alpha}_{\underline{k}} - \varrho^{*\alpha} \mathsf{J}^{*\alpha}_{\underline{ij}} \frac{s^*_i s^*_j}{2} U^{*\alpha}_{\underline{k}} \Bigg], \tag{6.103}$$

In spite of the similarity of these expressions with those found in the former sections, there is an interesting difference. To notice this, we first recall two trivial identities

$$\sum_{\alpha=1}^{N} \varrho^{*\alpha} v^{*\alpha}_i = \varrho^* v^*_i + \sum_{\alpha=1}^{N} \varrho^{*\alpha} C^{*\alpha}_{\underline{i}}, \qquad \sum_{\alpha=1}^{N} \varrho^{*\alpha} u^{*\alpha}_i = \varrho^* u^*_i + \sum_{\alpha=1}^{N} \varrho^{*\alpha} U^{*\alpha}_{\underline{i}}. \tag{6.104}$$

Due to (6.23), (6.92), $(6.97)_1$ and (6.99), there immediately follows that

$$\sum_{\alpha=1}^{N} \varrho^{*\alpha} C_i^{\overline{*}\alpha} = 0, \qquad \text{whereas, in general,} \qquad \sum_{\alpha=1}^{N} \varrho^{*\alpha} U_i^{\overline{*}\alpha} \neq 0. \quad (6.105)$$

This last result leads to the interesting conclusion that resultant diffusive mass fluxes on $\mathcal{S}^2$ are allowed in microstructured mixtures, being defined by the *net orientational diffusive mass flux density*

$$\varrho^* \Delta_i^* = \sum_{\alpha=1}^{N} \varrho^{*\alpha} U_i^{\overline{*}\alpha}. \quad (6.106)$$

The physical meaning of the flux $\varrho^* \Delta_i^*$ should not be misunderstood. Obviously, it cannot be conductive, since it represents a net mass transport in the orientation space (cf. Sect. 3.2). To verify that it cannot be convective either, one recalls that, according to the definition of convection discussed in Sect. 3.2, there cannot exist convective fluxes in a mixture which does not move. Since the motion of the mixture for any position, instant and orientation is described by the velocities v_i^* and s_i^*, defined in (6.4) and (6.23), we conclude from $(6.23)_2$ that no orientational convective flux can arise in the mixture when s_i^*, and consequently u_i^*, vanish. Hence, setting $u_i^* = 0$ in $(6.104)_2$, one concludes from (6.106) that $\varrho^* \Delta_i^*$ must be interpreted as an effective diffusive (non-convective and non-conductive) flux of mass on $\mathcal{S}^2$, which can only arise when neither the inertia tensors nor the spin velocities of all constituents oriented in a given direction are the same. In other words, the result above teaches us that the concept of *orientational convective flux of mass* is not always a synonym for *total mass transport on* $\mathcal{S}^2$.

From (6.92)–(6.106), the orientation-dependent balance equations for the mixture read in this case

$$\frac{\partial \varrho^*}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^* v_i^*\right) + \partial_i\left(\varrho^* u_i^* + \varrho^* \Delta_i^*\right) = \varrho^* \Gamma^*, \quad (6.107)$$

$$\frac{\partial \varrho^* v_i^*}{\partial t} + \frac{\partial}{\partial x_j}\left(\varrho^* v_i^* v_j^* - \mathsf{t}_{ij}^*\right) + \partial_j\left(\varrho^* v_i^* u_j^* + \varrho^* v_i^* \Delta_j^* - \boldsymbol{\tau}_{ij}^*\right) = \varrho^* \kappa_i^* + \varrho^* g_i^*, \quad (6.108)$$

$$\frac{\partial \varrho^* L_i^*}{\partial t} + \frac{\partial}{\partial x_j}\left(\varrho^* L_i^* v_j^* - \mathsf{M}_{ij}^*\right) + \partial_j\left(\varrho^* L_i^* u_j^* + \varrho^* L_i^* \Delta_j^* - \mathsf{X}_{ij}^*\right) = \varrho^* N_i^* + \varrho^* K_i^*, \quad (6.109)$$

$$\frac{\partial \varrho^* E^*}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^* E^* v_i^* + Q_i^*\right) + \partial_i\left(\varrho^* E^* u_i^* + \varrho^* E^* \Delta_i^* + \Xi_i^*\right) = \varrho^* P^* + \varrho^* R^*, \quad (6.110)$$

$$\frac{\partial \varrho^* \eta^*}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^* \eta^* v_i^* + \phi_i^*\right) + \partial_i\left(\varrho^* \eta^* u_i^* + \varrho^* \eta^* \Delta_i^* + \varphi_i^*\right) = \varrho^* \varsigma^* + \varrho^* s^*, \quad (6.111)$$

where (6.109) can be simplified to

$$\frac{\partial \varrho^* \sigma_i^*}{\partial t} + \frac{\partial}{\partial x_j}\left(\varrho^* \sigma_i^* v_j^* - \mathsf{m}_{ij}^*\right) + \partial_j\left(\varrho^* \sigma_i^* u_j^* + \varrho^* \sigma_i^* \Delta_j^* - \boldsymbol{\varpi}_{ij}^*\right) + \epsilon_{ijk} \mathsf{t}_{jk}^* = \varrho^* \nu_i^* + \varrho^* c_i^* \,. \quad (6.112)$$

Clearly, (6.107)–(6.112) are not identical to the equations for a single medium (6.51)–(6.56). Consequently, for the particular case of the *orientation dependent description* of mixtures with microstructure, the third metaphysical principle of Truesdell (see Footnote 5) fails to hold. However, this should not be surprising, as (6.51)–(6.56) and (6.107)–(6.112) must express such an orientational dependence for which these principles were originally not intended to apply. In any case, after integration of (6.107)–(6.112) over the whole $\mathcal{S}^2$, the contribution of orientational diffusive mass fluxes disappears and the balance equations for a microstructured mixture (6.60)–(6.65) are recovered, since (6.50) applies and the relations (6.57)–(6.59) and (6.66)–(6.70) remain valid. Therefore, all Truesdell's metaphysical principles are fulfilled in the ordinary description (i.e., after consideration of all orientations) and there occurs no "physical aberration" in the mixture behavior.

6.6 Jump conditions for single and mixed media

After the results presented in Sects. 6.3 to 6.5, it becomes straightforward to derive jump conditions appropriate for mixtures of microstructured media. Effectively, from (6.36) we derive the following orientation dependent jump conditions of mass, linear and angular momenta, energy and entropy, valid for every constituent α of the mixture:

$$\left[\!\left[\varrho^{*\alpha} \left(v_i^{*\alpha} - v_i^{\mathcal{W}} \right) \right]\!\right] e_i^{\mathcal{W}} = {}^{\varrho}\beta^{*\alpha} + {}^{\varrho}\zeta^{*\alpha}, \tag{6.113}$$

$$\left[\!\left[\varrho^{*\alpha} v_i^{*\alpha} \left(v_j^{*\alpha} - v_j^{\mathcal{W}} \right) - t_{ij}^{*\alpha} \right]\!\right] e_j^{\mathcal{W}} = {}^{v}\beta_i^{*\alpha} + {}^{v}\zeta_i^{*\alpha}, \tag{6.114}$$

$$\left[\!\left[\varrho^{*\alpha} L_i^{*\alpha} \left(v_j^{*\alpha} - v_j^{\mathcal{W}} \right) - M_{ij}^{*\alpha} \right]\!\right] e_j^{\mathcal{W}} = {}^{L}\beta_i^{*\alpha} + {}^{L}\zeta_i^{*\alpha}, \tag{6.115}$$

$$\left[\!\left[\varrho^{*\alpha} E^{*\alpha} \left(v_i^{*\alpha} - v_i^{\mathcal{W}} \right) + Q_i^{*\alpha} \right]\!\right] e_i^{\mathcal{W}} = {}^{E}\beta^{*\alpha} + {}^{E}\zeta^{*\alpha}, \tag{6.116}$$

$$\left[\!\left[\varrho^{*\alpha} \eta^{*\alpha} \left(v_i^{*\alpha} - v_i^{\mathcal{W}} \right) + \phi_i^{*\alpha} \right]\!\right] e_i^{\mathcal{W}} = {}^{\eta}\beta^{*\alpha} + {}^{\eta}\zeta^{*\alpha}. \tag{6.117}$$

Moreover, Eq. (6.115) can be rewritten with the help of $(6.45)_1$, $(6.47)_1$ and (6.114) as

$$\left[\!\left[\varrho^{*\alpha} \sigma_i^{*\alpha} \left(v_j^{*\alpha} - v_j^{\mathcal{W}} \right) - m_{ij}^{*\alpha} \right]\!\right] e_j^{\mathcal{W}} = {}^{\sigma}\beta_i^{*\alpha} + {}^{\sigma}\zeta_i^{*\alpha}, \tag{6.118}$$

where

$${}^{\sigma}\beta_i^{*\alpha} = {}^{L}\beta_i^{*\alpha} - \epsilon_{ijk} x_j \, {}^{v}\beta_k^{*\alpha}, \qquad \text{and} \qquad {}^{\sigma}\zeta_i^{*\alpha} = {}^{L}\zeta_i^{*\alpha} - \epsilon_{ijk} x_j \, {}^{v}\zeta_k^{*\alpha}. \tag{6.119}$$

It is worthwhile to remark that, as in ordinary media, no jump condition of the form (6.36) can be derived for the internal energy, since the assumption of bounded limit values on each side of the singular surface cannot be always fulfilled by its production terms. The reason is the explicit dependence of the production of internal energy on gradients of translational and angular velocities which may be unbounded when $v_i^{*\alpha}$ and $s_i^{*\alpha}$ suffer jumps across the surface.

Similar expressions for the constituents of the mixture and its orientation dependent description can be easily derived from (6.113)–(6.117) through integration over all orientations and sum over all constituents, respectively. Hence, from (6.77)–(6.79) and (6.92)–(6.94) we find

❑ after summation:

$$\left[\!\left[\varrho^* \left(v_i^* - v_i^{\mathcal{W}}\right) \right]\!\right] e_i^{\mathcal{W}} = {}^{\varrho}\beta^* + {}^{\varrho}\zeta^*, \tag{6.120}$$

$$\left[\!\left[\varrho^* v_i^* \left(v_j^* - v_j^{\mathcal{W}}\right) - t_{ij}^* \right]\!\right] e_j^{\mathcal{W}} = {}^{v}\beta_i^* + {}^{v}\zeta_i^*, \tag{6.121}$$

$$\left[\!\left[\varrho^* L_i^* \left(v_j^* - v_j^{\mathcal{W}}\right) - M_{ij}^* \right]\!\right] e_j^{\mathcal{W}} = {}^{L}\beta_i^* + {}^{L}\zeta_i^*, \tag{6.122}$$

$$\left[\!\left[\varrho^* E^* \left(v_i^* - v_i^{\mathcal{W}}\right) + Q_i^* \right]\!\right] e_i^{\mathcal{W}} = {}^{E}\beta^* + {}^{E}\zeta^*, \tag{6.123}$$

$$\left[\!\left[\varrho^* \eta^* \left(v_i^* - v_i^{\mathcal{W}}\right) + \phi_i^* \right]\!\right] e_i^{\mathcal{W}} = {}^{\eta}\beta^* + {}^{\eta}\zeta^*, \tag{6.124}$$

$$\left[\!\left[\varrho^* \sigma_i^* \left(v_j^* - v_j^{\mathcal{W}}\right) - m_{ij}^* \right]\!\right] e_j^{\mathcal{W}} = {}^{\sigma}\beta_i^* + {}^{\sigma}\zeta_i^* \,. \tag{6.125}$$

$$\tag{6.126}$$

❑ after integration:

$$\left[\!\left[\varrho^{\alpha} \left(v_i^{\alpha} - v_i^{\mathcal{W}}\right) \right]\!\right] e_i^{\mathcal{W}} = {}^{\varrho}\beta^{\alpha} + {}^{\varrho}\zeta^{\alpha}, \tag{6.127}$$

$$\left[\!\left[\varrho^{\alpha} v_i^{\alpha} \left(v_j^{\alpha} - v_j^{\mathcal{W}}\right) - t_{ij}^{\alpha} \right]\!\right] e_j^{\mathcal{W}} = {}^{v}\beta_i^{\alpha} + {}^{v}\zeta_i^{\alpha}, \tag{6.128}$$

$$\left[\!\left[\varrho^{\alpha} L_i^{\alpha} \left(v_j^{\alpha} - v_j^{\mathcal{W}}\right) - M_{ij}^{\alpha} \right]\!\right] e_j^{\mathcal{W}} = {}^{L}\beta_i^{\alpha} + {}^{L}\zeta_i^{\alpha}, \tag{6.129}$$

$$\left[\!\left[\varrho^{\alpha} E^{\alpha} \left(v_i^{\alpha} - v_i^{\mathcal{W}}\right) + Q_i^{\alpha} \right]\!\right] e_i^{\mathcal{W}} = {}^{E}\beta^{\alpha} + {}^{E}\zeta^{\alpha}, \tag{6.130}$$

$$\left[\!\left[\varrho^{\alpha} \eta^{\alpha} \left(v_i^{\alpha} - v_i^{\mathcal{W}}\right) + \phi_i^{\alpha} \right]\!\right] e_i^{\mathcal{W}} = {}^{\eta}\beta^{\alpha} + {}^{\eta}\zeta^{\alpha}, \tag{6.131}$$

$$\left[\!\left[\varrho^{\alpha} \sigma_i^{\alpha} \left(v_j^{\alpha} - v_j^{\mathcal{W}}\right) - m_{ij}^{\alpha} \right]\!\right] e_j^{\mathcal{W}} = {}^{\sigma}\beta_i^{\alpha} + {}^{\sigma}\zeta_i^{\alpha} \,, \tag{6.132}$$

where (6.125) and (6.132) have been derived from (6.122) and (6.129) with the help of $(6.45)_1$, $(6.47)_1$, (6.121) and (6.128). Further,

$${}^{K}\beta^* = \sum_{\alpha=1}^{N} {}^{K}\beta^{*\alpha}, \quad {}^{K}\zeta^* = \sum_{\alpha=1}^{N} {}^{K}\zeta^{*\alpha}, \quad {}^{K}\beta^{\alpha} = \oint_{\mathcal{S}^2} {}^{K}\beta^{*\alpha}\, d^2n, \quad {}^{K}\zeta^{\alpha} = \oint_{\mathcal{S}^2} {}^{K}\zeta^{*\alpha}\, d^2n, \tag{6.133}$$

$${}^{L}\beta_i^* = \sum_{\alpha=1}^{N} {}^{L}\beta_i^{*\alpha}, \quad {}^{L}\zeta_i^* = \sum_{\alpha=1}^{N} {}^{L}\zeta_i^{*\alpha}, \quad {}^{L}\beta_i^{\alpha} = \oint_{\mathcal{S}^2} {}^{L}\beta_i^{*\alpha}\, d^2n, \quad {}^{L}\zeta_i^{\alpha} = \oint_{\mathcal{S}^2} {}^{L}\zeta_i^{*\alpha}\, d^2n, \tag{6.134}$$

with $\mathsf{K} = \{\varrho, E, \eta\}$ and $\mathsf{L} = \{v, L, \sigma\}$. It should be noticed that (6.120)–(6.125) are identical to the jump conditions for single microstructured media, which can be obtained by setting $N = 1$ in (6.113)–(6.118).

Finally, one can derive the jump conditions for the mixture from (6.120)–(6.132) after performing either the integration on $\mathcal{S}^2$ of the conditions (6.120)–(6.125), or the summation over all constituents of the conditions (6.126)–(6.132). Hence, from (6.57)–(6.59) or (3.43)–(3.45) follow

$$\left[\!\left[\varrho \left(v_i - v_i^{\mathcal{W}} \right) \right]\!\right] e_i^{\mathcal{W}} = {}^{\varrho}\beta + {}^{\varrho}\zeta, \tag{6.135}$$

$$\left[\!\left[\varrho v_i \left(v_j - v_j^{\mathcal{W}} \right) - t_{ij} \right]\!\right] e_j^{\mathcal{W}} = {}^{v}\beta_i + {}^{v}\zeta_i, \tag{6.136}$$

$$\left[\!\left[\varrho L_i \left(v_j - v_j^{\mathcal{W}} \right) - M_{ij} \right]\!\right] e_j^{\mathcal{W}} = {}^{L}\beta_i + {}^{L}\zeta_i, \tag{6.137}$$

$$\left[\!\left[\varrho E \left(v_i - v_i^{\mathcal{W}} \right) + Q_i \right]\!\right] e_i^{\mathcal{W}} = {}^{E}\beta + {}^{E}\zeta, \tag{6.138}$$

$$\left[\!\left[\varrho \eta \left(v_i - v_i^{\mathcal{W}} \right) + \phi_i \right]\!\right] e_i^{\mathcal{W}} = {}^{\eta}\beta + {}^{\eta}\zeta, \tag{6.139}$$

and Eq. (6.137) can be rewritten with the help of $(6.45)_1$, $(6.47)_1$ and (6.136) as

$$\left[\!\left[\varrho \sigma_i \left(v_j - v_j^{\mathcal{W}} \right) - m_{ij} \right]\!\right] e_j^{\mathcal{W}} = {}^{\sigma}\beta_i + {}^{\sigma}\zeta_i, \tag{6.140}$$

where

$${}^{\mathsf{K}}\beta = \sum_{\alpha=1}^{N} {}^{\mathsf{K}}\beta^{\alpha} = \oint_{\mathcal{S}^2} {}^{\mathsf{K}}\beta^{*}\, d^2n, \qquad {}^{\mathsf{K}}\zeta = \sum_{\alpha=1}^{N} {}^{\mathsf{K}}\zeta^{\alpha} = \oint_{\mathcal{S}^2} {}^{\mathsf{K}}\zeta^{*}\, d^2n, \tag{6.141}$$

$${}^{\mathsf{L}}\beta_i = \sum_{\alpha=1}^{N} {}^{\mathsf{L}}\beta_i^{\alpha} = \oint_{\mathcal{S}^2} {}^{\mathsf{L}}\beta_i^{*}\, d^2n, \qquad {}^{\mathsf{L}}\zeta_i = \sum_{\alpha=1}^{N} {}^{\mathsf{L}}\zeta_i^{\alpha} = \oint_{\mathcal{S}^2} {}^{\mathsf{L}}\zeta_i^{*}\, d^2n, \tag{6.142}$$

with (again) $\mathsf{K} = \{\varrho,\, E,\, \eta\}$ and $\mathsf{L} = \{v,\, L,\, \sigma\}$.

Part III

Mixtures with Continuous Diversity: Applications

From Polymers to Icebergs

7. Polymeric Solutions

Entropy, *a much overused and abused physical concept from thermodynamics, has been applied to everything from the initial fireball to the totalitarian state.*

Anthony F. Aveni, [17] p. 156

The potential of the theory of mixtures with continuous diversity can be remarkably illustrated through the thermodynamic analysis of induced anisotropy in rigid rodlike polymer solutions. Indeed, different concentration regimes can equally be considered and the results of the constitutive theory are enlightening. Among other interesting inferences of the constitutive theory, it is shown that the microstructure evolution is governed by a hyperbolic equation (and not a parabolic one, as could be supposed), which after suppression of inertial effects reduces to a non-linear evolution equation of the Fokker–Planck type. Finally, an analogy between the results derived by this continuum approach and those usually obtained from statistical theories is established, by particularizing the predictions for ideal solutions.

7.1 Why bother with microstructure evolution?

Five years prior to Weissenberg's presentation [424, 425] of his striking photographs illustrating normal stress effects in steady flows to the participants of the "First International Congress of Rheology" in Scheweningen, 1948, Merrington [303] was already reporting about the swelling phenomenon in steady flows from tubes. During the same period, many other accounts of "abnormal flow phenomena", such as elastic recovery and stress relaxation, became available in the literature[1] [157, 185, 186, 423–425].

This happened at the end of the Second World War, when the technological revolution caused by the development of new complex materials promoted a strong impact upon the research on rheology and fluid mechanics. As commented by Wilmański [433]:

> "*During the Second World War the discovery of napalm (na(phthene) + palm(itate)) started the development of fluid models capable of describing the motion of such substances. It was observed that during the extrusion from pipes some fluids, for example napalm, increase their cross-section in contrast*

[1] For an extensive bibliography of the early works on this subject, see [408].

> *to normal viscous Newtonian fluids. Fortunately, this property is characteristic not only for napalm but also for numerous other less harmful fluids ...*"
>
> (p. 141)

Whereas the occurrence of normal stress effects ultimately confirmed the existence of deviations from the usual Newtonian behavior – a fact up to that time still refused by some old-line researchers – it was not completely clear where such kind of strange phenomena, generically called *viscoelastic effects*, really come from. The controversy about the origins of fluid viscoelasticity continued for a long time, and an exposition of it has taken many pages of the memoir by Truesdell & Noll [408]. In particular, a good illustration of this discussion lies on an acid comment found in that treatise:

> "*Actually, the climbing phenomenon (sometimes called Weissenberg effect) itself was not new, since rotary stirrers had long ago been found inadequate for paints, but it was not understood that simple mechanical principles suffice to explain it. Likewise, the phenomenon of swelling on extrusion from a tube was known in the artificial fibre industry but thought to be of chemical or 'plastic' origin or was subsumed under that turgid euphemism for ignorance, 'thixotropy'.*"
>
> (p. 453)

To tell the truth, the intimate relation between elasticity and viscosity has been known in Physics since the time of Maxwell [296], who successfully explained the phenomenon of viscosity as a combination of elasticity with a relaxation effect. Starting from this idea, he arrived at one of the first and most popular models of viscoelasticity, which bears his name. Succinctly, he proposed a one-dimensional stress–strain relation of the type[2]

$$\dot{\sigma} = \mu\dot{\gamma} - \frac{\sigma}{\tau} \,, \tag{7.1}$$

which after some rearrangement can be rewritten as

$$\sigma = \eta\dot{\gamma} - \tau\dot{\sigma} \,, \tag{7.2}$$

where σ denotes a stress of some kind, $\dot{\sigma}$ its time rate, γ the strain, $\dot{\gamma}$ the strain rate, μ an elastic modulus, τ a relaxation time and $\eta = \mu\tau$ the viscosity. As can be easily seen, for $\tau \to \infty$ Eq. (7.1) reduces to the simple elastic relation $\sigma = \mu\gamma$, while for $\tau \to 0$, η fixed, Eq. (7.2) becomes the usual expression for the viscous stress $\sigma = \eta\dot{\gamma}$.

The geniality of Maxwell's explanation of the viscosity phenomenon should not be obscured by its apparent simplicity. In fact, it had (and has) inspired most of the important subsequent works on viscoelasticity and related topics. For example, it was the basis for Noll's theory of hygrosteric materials [324], which includes, among others, the hypo-elastic theory of Truesdell [404] as a special case.

On the other hand, the concept of stress relaxation and the linear nature of the Maxwell's model, which enables a superposition of elastic and viscous effects, was

[2]The symbols σ, γ and τ found in (7.1) and (7.2) have solely illustrative character, and should therefore not be confused with the standard notation employed in other parts of this work.

generalized by Boltzmann [48] in his linear accumulative theory, which in turn led later to the well-known theory of materials with memory [180–182, 340]. The relationship between the memory and the elasticity of a viscoelastic fluid was qualitatively well illustrated by Pao [340]:

> "*In normal viscous fluids, only the rate of deformation is of interest. In the absence of external and body forces, no stresses are developed and there is no means of distinguishing between a natural (undeformed) state and a deformed state. ... (In a viscoelastic fluid) the natural state of the fluid changes constantly in flow and tries to catch up with the instantaneous state or the deformed state. It never does quite succeed in doing so, and the lag is a measure of the memory or elasticity. In elastic solids, the natural state does not change and there is perfect memory.*" (Sect. 1)

Moreover, the viscoelastic theory of Maxwell introduced one of the first constitutive equations of the "rate type" for the stress in a fluid, which are even nowadays the most useful type of constitutive equations for viscoelastic fluids (obviously at the present time in non-linear and other more complicated forms). Because of the linearity of the Maxwell model, it becomes trivial to derive a mechanical analog of it with a spring–dashpot system of the type given in fig. 7.1, which is often invoked for didactical purposes.

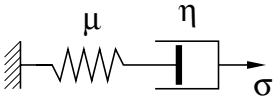


Fig. 7.1. The "in series" spring–dashpot element representing Maxwell's model. The quantities μ, η and σ are defined in (7.1)

From this mechanical representation immediately follows that other spring–dashpot combinations may be also possible: in fact, they have been used to construct numerous linear viscoelastic models for fluids and solids[3] (see fig. 7.2). For polymeric liquids, these simple mechanical analogs served earlier also to suggest, at least qualitatively, a connection between the elasticity of the suspended particles (e.g. macromolecules) and the abnormal rheological behavior of such solutions[4]

Theories which relate the macroscopic response of the fluid to the structure and mechanical properties of its molecules are usually called of *molecular* (or *kinetic*) type. The name *statistical rheology* is sometimes also employed when referring to them. Roughly, these theories describe the bulk behavior of the polymeric fluid in terms of its molecular structure, using methods of statistical mechanics. Because the molecular and hydrodynamic interactions play a decisive role in such statistical descriptions, one must distinguish between polymer melts, dilute, semi-dilute and concentrated solutions, which makes things even more complicated. The best known

[3] A beautiful exposition of these mechanical representations of linear viscoelastic materials, with a detailed analysis of their behavior, can be found in Chapter 10 of the treatise by Giesekus [158].

[4] See for example the network theories for rubberlike solids of Green & Tobolsky [183] and for polymeric liquids by Yamamoto & Inagaki and Lodge (presented in [280]). There are also illustrative descriptions in the book by Giesekus [158].

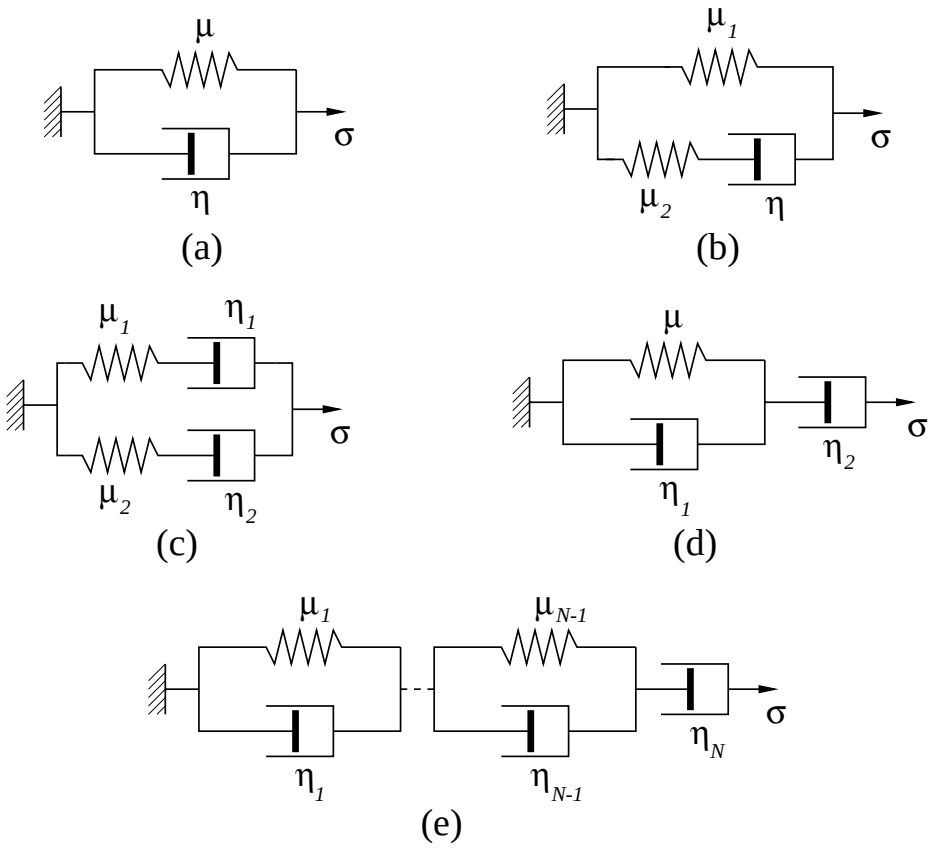


Fig. 7.2. Some spring–dashpot elements for viscoelastic models: (a) Kelvin–Voigt solid; (b) Poynting–Thomson solid; (c) Burgers fluid; (d) Jeffreys fluid; (e) "2N-1 parameter" fluid.

pioneering works on the molecular description of dilute polymeric liquids are related to the theories by Kirkwood–Auer (rigid rods) and Rouse–Zimm ("bead–spring" chain). They were also adapted by many authors, with the aim at describing different types of polymer molecules (freely joint bed–rod chains, rigid ellipsoids or dumbbells, semi-flexible rods, etc.). A review of such theories, as well as an extensive bibliography of the subject can be found in many textbooks of polymer dynamics, like the classical treatises by Ferry [136], Bird et al. [43, 44] and Doi & Edwards [103].

The success of molecular models, when compared to continuum theories, lies undoubtedly upon their simple explanation for complex rheological phenomena. For instance, the mystic "memory" of a viscoelastic polymer solution turns to be, from a molecular point of view, a simple outcome of thermal agitation of the suspended molecules, which interact by collision with other suspended molecules and hydrodynamically with the carrier fluid (see e.g. [103]). In this sense, solutions of rigid rodlike macromolecules are particularly instructive, since in this case the viscoelasticity does not depend on intrinsic properties of the molecules, like their flexibility or possibility of multiple equilibrium configurations – it is the evolution of the spatial and orientational distribution of rods which plays the fundamental role.

When rigid rodlike polymer molecules are suspended in a carrier liquid (like some polypeptides in suitable helicogenic solvents [136, 437]), complex microstructures

can be induced by flow, affecting the material response of the fluid in several ways. For instance, stream induced anisotropy can be optically measured by flow birefringence [330, 348, 349] and dynamic light scattering [38, 263, 437]. In fact, the instantaneous configuration of these polymeric suspensions is determined not only by the position of fluid particles, but in addition also by the orientational distribution of the identical rodlike molecules which constitute its microstructure.

Motivated by this microstructural picture, Kirkwood and co-workers [245, 246, 363] studied in a series of papers (within the frames of statistical rheology) the flow of dilute suspensions of rodlike macromolecules, basing on early works of Jeffery [231], Burgers [62] and Kuhn & Kuhn [253]. These were followed, among others, by the works by Prager [355], Kotaka [248], Doi & Edwards [102], Dahler and co-workers [86, 137] and Doi[100, 101], which progressively extended the range of the molecular theory to semidilute and concentrated regimes. An extensive survey of the literature on statistical rheology and molecular theories of polymeric fluids can be found in the treatises by Ferry [136], Bird et al. [43], Doi & Edwards [103], Larson [257] and Beris & Edwards [36]. In addition, the research on dilute and semidilute suspensions of slender rigid bodies has been reviewed by Brenner [56] and Petrie [350]. Worthy of notice is also the series of papers by Hinch & Leal [207, 208, 260, 261]. Common to all microscopic approaches cited above is the adoption of an *orientational distribution function* to describe the microstructure configuration of the fluid.

On the other hand, the analogy between a microstructured medium and a multicomponent mixture was mainly evidenced by Prager [354] and Curtiss [84]. The first author observed that, when dealing with translational diffusion of suspended rod-shaped particles, a group of randomly oriented rods should behave fairly like a mixture of species with different diffusion coefficients. Curtiss went further and, by deriving a kinetic theory for a gas of rigid non-spherical molecules, he showed that many relations were similar to the expressions for a mixture made up of an infinite number of components of continuously varying properties, and then he exploited this analogy to construct a solution of the Boltzmann equation. Some years later, also Dahler [85] emphasized this equivalence, by asserting that: "*This formal analogy is not only an interpretative device of considerable value, but* [...] *also* [...] *a practical tool ...*" (p. 1455). Finally, Condiff & Brenner [78] designated this equivalence a "dichotomy of representation" and employed it in combination with some fundamentals of the thermodynamics of irreversible processes to construct the first mixture-motivated phenomenological theory of suspensions of orientable particles.

Curiously, not much attention was devoted to this theme from that time on, despite the drastic progress achieved in the continuum thermodynamics of mixtures. In fact, within the frames of phenomenological approaches there always prevailed the description of microstructural dynamics by means of tensorial measures associated to observable anisotropic phenomena of optical and thermomechanical character. Such a type of description has a long tradition in continuum theories, dating back

at least to the turn of the 20th century[5] and being commonly associated to the names of Duhem [108] and the Cosserat brothers [79]. The cited tensorial measures were at the beginning one or several unit vectors called directors [120, 270, 409] (in the classical case, a rigid triad of them [108]), but later more elaborate descriptions using structure tensors (also called order, alignment or conformation tensors) became available [197, 287, 293].

Whilst the connection between the orientational distribution function of statistical physics and the tensorial measures of phenomenological approaches was already known in the domain of molecular theories for a long time (through the so-called "moments of the distribution function"), a concept somewhat equivalent to the orientational distribution function was formally introduced in continuum thermodynamics at a much slower pace. In some sense, it could be traced back to Condiff & Brenner [78]. Actually, the essential idea proposed by these authors lies on a well-known concept of statistical rheology and kinetic theory, namely the consideration of a five-dimensional hyperspace, which is nothing else than the product of the Euclidean space $\mathbb{R}^3$ and the two-dimensional *orientation space*, defined by the surface of the unitary sphere $\mathcal{S}^2$ (see Sect. 6.2). At any instant of time t, a particle of the medium is identified in $\mathbb{R}^3 \times \mathcal{S}^2$ by a composition of coordinates, related to the independent Cartesian components of the position vector x_i and the (normalized) orientation vector n_j, radial to the spherical surface of $\mathcal{S}^2$. Contrary to the directors of the Cosserat continua, the orientation vector has no direct relation to any directional property of the medium; in other words, it is not attached to any material particle. Consequently, one can regard the reference to n_j in $\mathcal{S}^2$ as the orientational counterpart to the spatial (Eulerian) description in the usual physical space $\mathbb{R}^3$.

7.2 Polymer suspensions as mixtures with continuous diversity

From the considerations above, the correspondence between the five-dimensional description of the microstructure and the theory of mixtures with continuous diversity presented in the foregoing Chapters becomes clear. For instance, one may define for any monodisperse and homogeneous suspension[6] of rigid rodlike polymers the *species mass density* $\varrho^*(x_i, t, n_j)$,[7] which represents the mass density at position x_i and time t of the species defined by the orientation n_j. In accordance with $(5.20)_1$, the mass density of the medium (i.e., of the "mixture of orientations") is given by

[5] It is virtually impossible to define the origins of most fundamental concepts, as e.g. oriented and microstructured media, which in practice seem to have grown slowly along decades of implicit assumptions, indefinite suggestions and obscure formulations, proffered by both famous and anonymous authors. References to some celebrated works serve mostly to give a "past", or "lineage", for such concepts; i.e. to situate them in the history.

[6] For inhomogeneous suspensions one should necessarily distinguish between the fields of mass density and polymer concentration; on the other hand, polydispersity would imply on an additional dimension to the space–assemblage, related to the length distribution of the polymer chains. Such features, although tractable, will not be considered in this simple version of the theory.

[7] As a matter of fact, the orientation vector has only two independent components, since it is normalized. For simplicity, however, the notation n_j will be maintained, together with the constraint $n_k n_k = 1$.

$$\varrho(x_i,t) = \oint_{\mathcal{S}^2} \varrho^*(x_k,t,n_j)\,\mathrm{d}^2 n\ , \tag{7.3}$$

integration being performed over the whole spherical surface of $\mathcal{S}^2$. Equation (7.3) expresses the fact that the monodisperse solution is considered, from a chemical point of view, a *single-component medium*, since the mass density of a given species ϱ^* does not resolve the fluid into solvent and solute parts. Consequently, suspensions of rigid rodlike polymers are to be modelled here as single component microstructured fluids for which balance equations have already been thoroughly studied in Chap. 6, Level ❶.

Effectively, in the absence of chemical reactions and mass supplies, there follows from (6.51) the species mass balance equation

$$\frac{\partial \varrho^*}{\partial t} + \frac{\partial \varrho^* v_i^*}{\partial x_i} + \partial_i\left(\varrho^* u_i^*\right) = 0\ , \tag{7.4}$$

where u_i^* is called the vector of species transition rate (see Sect. 5.2) and v_i^* is the usual species translational velocity, while

$$\partial_i\ = \frac{\partial}{\partial n_i} - n_i n_j \frac{\partial}{\partial n_j} \tag{7.5}$$

denotes the *orientational gradient operator*[8]. Its peculiar form results from the explicit consideration of the normalization condition[9] $n_k n_k = 1$. A further consequence of this normalization is the identity $n_i u_i^* = 0$, which allows one to rewrite the transition rate (cf. Sect. 5.2) as

$$u_i^* = \epsilon_{ijk} s_j^* n_k = \mathsf{S}_{ik}^* n_k\ , \qquad \text{with} \quad \mathsf{S}_{ik}^* = \epsilon_{kij} s_j^*\ . \tag{7.6}$$

In the definition above, $s_i^*(x_j,t,n_k)$ denotes the *species spin velocity* (i.e., the microstructural angular velocity), while S_{ik}^* represents its respective skew-symmetric tensor. It should be observed that (7.6) does not specify the component of species spin velocity parallel to n_i. Insofar as needle-like polymer molecules are considered, it seems natural to assume that these molecules will tend to rotate about their long-axis with the fluid in which they are embedded, that is

$$s_i^* n_i = \frac{1}{2} n_i\, \epsilon_{ijk} \frac{\partial v_k}{\partial x_j}. \tag{7.7}$$

The adoption of (7.6) and (7.7) allows a simple statistical interpretation of s_i^* as the angular velocity average of the suspended molecules instantaneously located in x_i and oriented in the n_i direction.

By introducing the *co-transitional time derivative*

[8] The gradient operator in $\mathcal{S}^2$ is occasionally defined by certain authors in a somewhat different manner as $\epsilon_{ijk} n_j\, \partial/\partial n_k$, see e.g. [78].

[9] Indeed, with reference to a polar coordinate system, the components of ∂_i can be readily obtained from the components of the usual gradient operator in $\mathbb{R}^3$ by simply discarding the radial term and assuming the normalization condition for the radius vector [36, 78].

$$\grave{\mathsf{A}}^{*} = \frac{\partial \mathsf{A}^{*}}{\partial t} + v_i^{*}\,\frac{\partial \mathsf{A}^{*}}{\partial x_i} + u_k^{*}\,\partial_k \mathsf{A}^{*}, \tag{7.8}$$

where A^{*} denotes some arbitrary tensor field, eq. (7.4) can be rewritten as

$$\grave{\varrho}^{*} + \varrho^{*}\frac{\partial v_i^{*}}{\partial x_i} + \varrho^{*}\partial_k u_k^{*} = 0. \tag{7.9}$$

As expected, with the aid of (6.33), (7.3) and revoking the usual definition of barycentric velocity of the "mixture", namely (cf. $(5.20)_2$)

$$v_i(x_j,t) = \frac{1}{\varrho}\oint\limits_{\mathcal{S}^2} \varrho^{*}(x_k,t,n_l)v_i^{*}(x_p,t,n_q)\,d^2n, \tag{7.10}$$

one can retrieve the usual equation of continuity (3.53), after integration of (7.4) over the whole orientation space $\mathcal{S}^2$.

The definition of co-transitional time derivative (7.8) allows one to rewrite the balance equations of linear momentum (6.52) and spin (6.56) respectively as

$$\varrho^{*}\grave{v}_i^{*} - \frac{\partial \mathsf{t}_{ij}^{*}}{\partial x_j} - \partial_j \boldsymbol{\tau}_{ij}^{*} = \varrho^{*}\left(\kappa_i^{*} + g_i^{*}\right), \tag{7.11}$$

and

$$\varrho^{*}\left(\mathsf{I}_{ij}^{*}s_j^{*}\right)\grave{} - \frac{\partial \mathsf{m}_{ij}^{*}}{\partial x_j} - \partial_j \boldsymbol{\varpi}_{ij}^{*} + \epsilon_{ijk}\mathsf{t}_{jk}^{*} = \varrho^{*}\left(c_i^{*} + \nu_i^{*}\right), \tag{7.12}$$

with I_{ij}^{*}, t_{ij}^{*}, m_{ij}^{*}, $\boldsymbol{\tau}_{ij}^{*}$, $\boldsymbol{\varpi}_{ij}^{*}$, κ_i^{*}, ν_i^{*}, g_i^{*} and c_i^{*} denoting the species fields of specific inertia tensor, Cauchy stress, Voigt couple stress, orientational stress and couple stress, specific interaction force and couple, specific external force and couple, respectively. Besides, provided that the macromolecules which constitute the microstructure are viewed as slender rods, there hold the expressions

$$\mathsf{I}_{ij}^{*} = R^2\left(\delta_{ij} - n_i n_j\right) \qquad \text{and consequently} \qquad \grave{\mathsf{I}}_{kl}^{*} = -(u_k^{*}n_l + u_l^{*}n_k)\,, \tag{7.13}$$

where R is a molecular inertial constant.

Subtraction of (7.11) and (7.12) from (6.54) yields the balance equation of internal energy

$$\begin{aligned}\varrho^{*}\grave{e}^{*} + \frac{\partial q_j^{*}}{\partial x_j} - \mathsf{t}_{ij}^{*}\frac{\partial v_i^{*}}{\partial x_j} - \mathsf{m}_{ij}^{*}\frac{\partial s_i^{*}}{\partial x_j} + \partial_j \xi_j^{*} - \boldsymbol{\tau}_{ij}^{*}\partial_j v_i^{*} - \\ -\boldsymbol{\varpi}_{ij}^{*}\partial_j s_i^{*} - \epsilon_{ijk}s_i^{*}\mathsf{t}_{jk}^{*} = \varrho^{*}\left(\varepsilon^{*} + r^{*}\right)\,,\end{aligned} \tag{7.14}$$

where e^{*}, q_j^{*}, ξ_j^{*} ε^{*} and r^{*} denote the species fields of specific internal energy, spatial and orientational heat fluxes, specific production of internal energy and radiation supply, respectively.

Finally, from (6.55), (7.8), (7.9) and the preceding arguments, there immediately follows the entropy balance equation

$$\varrho^{*}\grave{\eta}^{*} + \frac{\partial \phi_i^{*}}{\partial x_i} + \partial_i \varphi_i^{*} = \varrho^{*}\varsigma^{*} + \varrho^{*}s^{*}\,, \tag{7.15}$$

where η^{*}, ϕ_i^{*}, φ_i^{*}, ς^{*} and s^{*} are the species fields of specific entropy, its spatial and orientational fluxes, entropy production and its external supply.

7.3 Constitutive relations

A thermodynamic process in an homogeneous monodisperse solution of rigid rodlike polymers will be characterized by the fields of (cf. (6.1))

$$\begin{aligned} &\text{mass density} && \varrho^*(x_i,t,n_j)\ ,\\ &\text{translational velocity} && v_i^*(x_j,t,n_k)\ ,\\ &\text{spin velocity} && s_i^*(x_j,t,n_k)\ ,\\ &\text{temperature} && T(x_i,t)\ . \end{aligned} \tag{7.16}$$

Notice that the above choice of fields does not completely coincide with (6.1). A partial justification is that the adoption of temperature as a basic field may be advantageous as long as the temperature does not depend upon orientation, for given position and time instant (see Footnote 1). Further, the use of spin velocity, instead of spin, in the list (7.16) is driven merely by aesthetics: it will facilitate the latter comparison with works of other authors.

It is immediate to recognize that, at this stage, (7.9), (7.11), (7.12) and (7.14) cannot serve as a closed system for the basic fields (7.16), since these equations still contain many other unknown quantities. In fact, to close the system one has to consider these additional quantities as material functions, which are related to the basic fields through constitutive relations. Such relations are furthermore constrained by the entropy principle, as expressed by (5.15) and (7.15), as well as the axiom of frame indifference [73, 317, 408]. Thus, by considering a first order gradient theory, one can employ the rule of equipresence [275, 408] to propose the following isotropic constitutive functional form

$$\begin{aligned} \left\{\mathsf{t}_{ij}^*, \boldsymbol{\tau}_{ij}^*, \kappa_i^*, \mathsf{m}_{ij}^*, \boldsymbol{\varpi}_{ij}^*, \nu_i^*, e^*, q_i^*, \xi_i^*, \varepsilon^*, \eta^*, \phi_i^*, \varphi_i^*, \delta^*\right\} = \\ = \check{\mathsf{F}}\left(x_k, n_l, t; \varrho^\circ, T, v_m^\circ, \mathsf{S}_{no}^\circ, \frac{\partial \varrho^\circ}{\partial x_p}, \frac{\partial T}{\partial x_q}, \mathsf{D}_{rs}^\circ, \mathsf{W}_{tu}^\circ, \frac{\partial s_v^\circ}{\partial x_w}\right), \end{aligned} \tag{7.17}$$

where $\boldsymbol{Q}^\circ$ denotes the set of values of the arbitrary quantity $\boldsymbol{Q}^*$ in all points of the orientation space, i.e., $\boldsymbol{Q}^\circ = \{\boldsymbol{Q}^*(x_i,t,p_j) : p_j \in \mathcal{S}^2\}$, and

$$\mathsf{D}_{ij}^* = \frac{\partial v_{(i}^*}{\partial x_{j)}} = \frac{1}{2}\left(\frac{\partial v_i^*}{\partial x_j} + \frac{\partial v_j^*}{\partial x_i}\right), \qquad \mathsf{W}_{ij}^* = \frac{\partial v_{[i}^*}{\partial x_{j]}} = \frac{1}{2}\left(\frac{\partial v_i^*}{\partial x_j} - \frac{\partial v_j^*}{\partial x_i}\right) \tag{7.18}$$

denote the species tensor fields of strain rate and vorticity, respectively.

Of course, the functional (7.17) is quite general and too difficult to handle. Searching for a rather more modest description, one may impose the following simplifying assumptions:

1. Invariance of material response with respect to inversions of the orientation vector n_i (i.e., fore–aft symmetry: rodlike molecules oriented anti-parallel to each other are assumed to be indistinguishable);

2. Exclusion of the functional dependence on gradients of density, provided that the elastic energy effects characteristic of the liquid crystalline phases are beyond the scope of the present isotropic theory;
3. Linearization of (7.17) with respect to species spin velocity and all gradients of the basic fields;
4. Neglect of infinitesimal memory effects associated with the history of the entire microstructure configuration by switching $\mathsf{S}^{\circ}_{ij} \rightarrow \mathsf{S}^{*}_{ij}$ in the set of constitutive variables;
5. Exclusion of the functional dependence on gradients of the spin velocity, by assuming that S^{*}_{ij} is of the order of W^{*}_{ij} and, consequently, that $\partial s^{*}_{i}/\partial x_j$ is proportional to second order gradients;
6. Elision of translational diffusion effects by setting $v^{\circ}_{i} = v^{*}_{i} = v_i(x_j, t)$, in order to concentrate attention on the microstructure evolution driven by rotational diffusion phenomena.

The first two assumptions make clear that highly concentrated and optically active polymeric solutions are excluded from the present constitutive theory. Besides that, the latter restrictions are conspicuously stronger than the former ones.

Additionally, the constitutive dependence on the instantaneous microstructure configuration (given by ϱ°) will be approximated in a coarse, but effective manner, through the splitting of it in two independent variables. These are namely the species mass density ϱ^{*} at orientation n_i, and its complementary *structure parameter* β^{*}, conceived as a non-dimensional quantity which drafts the current microstructure configuration by accounting for the mass density of all species on $\mathcal{S}^2$, with reference to the particular orientation n_i. Generically, after introducing the species mass fraction

$$f^{*}(x_i, t, n_j) = \frac{\varrho^{*}}{\varrho} \, , \qquad \text{with} \qquad \oint_{\mathcal{S}^2} f^{*} \, \mathrm{d}^2 n = 1 \, , \tag{7.19}$$

the structure parameter can be defined by

$$\beta^{*}\left(x_i, t, n_j\right) = \oint_{\mathcal{S}^2} \mathsf{B}\big(f^{*}_{(p)}, p_m, f^{*}, n_q\big) \, d^2 p, \tag{7.20}$$

with the functional B so chosen as to ensure that β^{*} is independent of ϱ^{*}. As a consequence, this constraint implies the condition

$$\mathsf{B}\big(f^{*}_{(p)}, p_m, f^{*}, n_q\big)\Big|_{p_i = n_i} = 0, \tag{7.21}$$

where $f^{*}_{(p)} = f^{*}\left(x_k, t, p_l\right)$. The definite form of the functional B depends on the character of the relevant microstructure interactions, usually modelled from microscopic considerations. An explicit expression for the functional B will not be necessary in the constitutive theory developed here (an illustrative expression for B, associated with the so-called *entanglement interactions*, can be found in the specializations discussed later on).

After the simplifications above, (7.17) reads

$$\left\{\mathsf{t}^*_{ij}, \boldsymbol{\tau}^*_{ij}, \kappa^*_i, \mathsf{m}^*_{ij}, \boldsymbol{\varpi}^*_{ij}, \nu^*_i, e^*, q^*_i, \xi^*_i, \varepsilon^*, \eta^*, \phi^*_i, \varphi^*_i, \delta^*\right\} = \\ = \check{\mathsf{F}}\left(x_k, n_l, t; \varrho^*, T, \beta^*, v_m, \mathsf{S}^*_{no}, \frac{\partial T}{\partial x_q}, \mathsf{D}_{rs}, \mathsf{W}_{tu}\right). \quad (7.22)$$

Further restrictions upon the constitutive functional (7.22) are imposed by the *rule of frame indifference* (or *material objectivity*) [275, 317, 408]. It rests upon the frame invariance (objectivity) of the constitutive functions with respect to frame changes, which are given by the extended *Euclidean transformation*

$$\tilde{x}_i = \mathsf{O}_{ij} x_j + b_i, \qquad \tilde{t} = t + a, \qquad \tilde{n}_i = \mathsf{O}_{ij} n_j, \quad (7.23)$$

where $(\tilde{x}_i, \tilde{t}, \tilde{n}_j)$ and (x_i, t, n_j) denote position, time and orientation in two different frames of reference, with a representing an arbitrary time shift, while the time dependent vector and tensor valued functions $b_i(t)$ and $\mathsf{O}_{ij}(t)$ denote, respectively, the relative position of the two reference frames and an orthogonal transformation (more details are given in App. B).

By using standard arguments (see App. B), it is straightforward to obtain, with the aid of (7.23), the transformation rules

$$\tilde{v}_i = \dot{\mathsf{O}}_{ij} x_j + \mathsf{O}_{ij} v_j + \dot{b}_i, \qquad \tilde{\mathsf{D}}_{ij} = \mathsf{O}_{ik}\mathsf{O}_{jl}\mathsf{D}_{kl}, \quad (7.24)$$

$$\tilde{\mathsf{W}}_{ij} = \mathsf{O}_{ik}\mathsf{O}_{jl}\mathsf{W}_{kl} + \Omega_{ij}, \qquad \tilde{\mathsf{S}}^*_{ij} = \mathsf{O}_{ik}\mathsf{O}_{jl}\mathsf{S}^*_{kl} + \Omega_{ij}, \quad (7.25)$$

$$\tilde{T} = T, \qquad \frac{\partial \tilde{T}}{\partial \tilde{x}_i} = \mathsf{O}_{ik}\frac{\partial T}{\partial x_k}, \qquad \tilde{\varrho}^* = \varrho^*, \qquad \tilde{\beta}^* = \beta^*, \quad (7.26)$$

$$\tilde{\mathsf{t}}^*_{ij} = \mathsf{O}_{ik}\mathsf{O}_{jl}\mathsf{t}^*_{kl}, \qquad \tilde{\boldsymbol{\tau}}^*_{ij} = \mathsf{O}_{ik}\mathsf{O}_{jl}\boldsymbol{\tau}^*_{kl}, \qquad \tilde{\kappa}^*_i = \mathsf{O}_{ij}\kappa^*_j, \quad (7.27)$$

$$\tilde{\mathsf{m}}^*_{ij} = s\mathsf{O}_{ik}\mathsf{O}_{jl}\mathsf{m}^*_{kl}, \qquad \tilde{\boldsymbol{\varpi}}^*_{ij} = s\mathsf{O}_{ik}\mathsf{O}_{jl}\boldsymbol{\varpi}^*_{kl}, \qquad \tilde{\nu}^*_i = s\mathsf{O}_{ij}\nu^*_j, \quad (7.28)$$

$$\tilde{e}^* = e^*, \qquad \tilde{q}^*_i = \mathsf{O}_{ij} q^*_j, \qquad \tilde{\xi}^*_i = \mathsf{O}_{ij}\xi^*_j, \qquad \tilde{\varepsilon}^* = \varepsilon^*, \quad (7.29)$$

$$\tilde{\eta}^* = \eta^*, \qquad \tilde{\phi}^*_i = \mathsf{O}_{ij}\phi^*_j, \qquad \tilde{\varphi}^*_i = \mathsf{O}_{ij}\varphi^*_j, \qquad \tilde{\delta}^* = \delta^*, \quad (7.30)$$

where $\Omega_{ij} = \dot{\mathsf{O}}_{ik}\mathsf{O}_{jk}$, and $s = \operatorname{sign}\left[\det\left(\mathsf{O}_{ij}\right)\right]$, with $s = -1$ for improper transformations (inversions of frame), otherwise $s = 1$. Moreover, it should be recalled that

$$\delta_{ij} = \mathsf{O}_{ik}\mathsf{O}_{jk} = \mathsf{O}_{ik}\mathsf{O}_{jl}\delta_{kl} \qquad \text{and} \qquad \epsilon_{ijk} = s\mathsf{O}_{il}\mathsf{O}_{jm}\mathsf{O}_{kn}\epsilon_{lmn}. \quad (7.31)$$

Therefore, exploiting the frame-indifference principle in the usual manner, one can easily conclude that the constitutive functions (7.22) cannot depend explicitly on x_i, t, v_i, S^*_{ij} and W_{ij}, implying a reformulation of the constitutive functional (7.22) to

$$\left\{\mathsf{t}^*_{ij}, \boldsymbol{\tau}^*_{ij}, \kappa^*_i, \mathsf{m}^*_{ij}, \boldsymbol{\varpi}^*_{ij}, \nu^*_i, e^*, q^*_i, \xi^*_i, \varepsilon^*, \eta^*, \phi^*_i, \varphi^*_i, \delta^*\right\} = \\ = \hat{\mathsf{F}}\left(n_l, \varrho^*, T, \beta^*, \mathsf{H}^*_{mn}, \frac{\partial T}{\partial x_q}, \mathsf{D}_{rs}\right), \quad (7.32)$$

where H^*_{ij} is the species tensor field of *relative spin velocity*, defined by

$$\mathsf{H}^*_{ij}(x_l, t, n_k) = \mathsf{S}^*_{ij} - \mathsf{W}_{ij}. \tag{7.33}$$

It should be remarked that, due to (7.7) and $(7.18)_2$, $\epsilon_{ijk} n_i \mathsf{H}^*_{jk} = 0$.

Explicit forms for the constitutive functions defined in (7.32) are summarized in App. E. At this point, however, it may suffice to express explicitly only the constitutive dependence on the linearized variables D_{ij}, H^*_{ij} and $\partial T/\partial x_i$, viz.[10],

$$e^* = e^{*(1)} + e^{*I}_{ij}\mathsf{D}_{ij}, \qquad \eta^* = \eta^{*(1)} + \eta^{*I}_{ij}\mathsf{D}_{ij}, \qquad \varepsilon^* = \varepsilon^{*(1)} + \varepsilon^{*I}_{ij}\mathsf{D}_{ij}, \tag{7.34}$$

$$q^*_i = q^{*I}_{ij}\frac{\partial T}{\partial x_j}, \qquad \phi^*_i = \phi^{*I}_{ij}\frac{\partial T}{\partial x_j}, \qquad \kappa^*_i = \kappa^{*I}_{ij}\frac{\partial T}{\partial x_j}, \tag{7.35}$$

$$\nu^*_i = \nu^{*(1)}\epsilon_{ijk}H^*_{jk} + \nu^{*(2)}\epsilon_{ijk}n_j\mathsf{D}_{<kl>}n_l, \tag{7.36}$$

$$\varphi^*_i = \varphi^{*(1)}(n_i n_j - \delta_{ij})\mathsf{D}_{<jk>}n_k - \varphi^{*(2)}\mathsf{H}^*_{ij}n_j, \tag{7.37}$$

$$\xi^*_i = \xi^{*(1)}(n_i n_j - \delta_{ij})\mathsf{D}_{<jk>}n_k - \xi^{*(2)}\mathsf{H}^*_{ij}n_j, \qquad \mathsf{m}^*_{ij} = m^{*I}_{ijk}\frac{\partial T}{\partial x_k}, \tag{7.38}$$

$$\boldsymbol{\tau}^*_{ij} = \tau^{*I}_{ijk}\frac{\partial T}{\partial x_k}, \qquad \boldsymbol{\varpi}^*_{ij} = \varpi^*\epsilon_{ijk}n_k + \varpi^{*(1)}n_i\epsilon_{jkl}\mathsf{H}^*_{kl} + \varpi^{*I}_{ijkl}\mathsf{D}_{kl}, \tag{7.39}$$

$$\begin{aligned}\mathsf{t}^*_{ij} = &-\left(p^* + p^{*I}_{kl}\mathsf{D}_{kl}\right)\delta_{ij} + \sigma^* n_{<i}n_{j>} + \sigma^{*I}_{<ij>kl}\mathsf{D}_{kl} + \sigma^{*II}_{<ij>kl}\mathsf{H}^*_{kl} - \\ &- 2t^{*(1)}n_{[i}\mathsf{D}_{<j]k>}n_k - 2t^{*(2)}n_{[i}H^*_{j]k}n_k - t^{*(3)}\mathsf{H}^*_{ij},\end{aligned} \tag{7.40}$$

where the fore–aft symmetry of the molecules and the transformation properties (7.24)–(7.31) were already considered. Furthermore, in the representations above, all scalar transport coefficients are functions only of ϱ^*, T and β^*, while the tensorial ones present an additional dependence on the orientation n_i.

Finally, it should be remarked that no representation was proposed for δ^*. In fact, a linearization assumption for the entropy production deviation usually seems to be physically inconsistent. The reason is that this function is related by (5.14) to entropy production terms, which must be non-linear quantities even though the constitutive relations are assumed linear. The information enclosed in the non-linear part of δ^* could be called with no shame "the price of ignorance". Indeed, it is related to very complex microstructural interactions in non-dilute solutions, which are expected to be hardly described (when feasible) even by ingenious molecular models. As will be shown in the next sections, however, this price is actually not so high. The most important features of the material behavior can be derived without any reference to the non-linearity of δ^*, while for some simple cases the entropy production deviation can be readily neglected by plain physical arguments.

[10] Angular brackets indicate traceless symmetrization of the enclosed pair of indices, i.e. $Q_{<ij>} = Q_{(ij)} - \delta_{ij}Q_{kk}/3$.

7.4 Exploitation of the entropy inequality

Insertion of (7.15) into (5.15) leads to the entropy inequality

$$\varrho^*\dot{\eta}^* + \frac{\partial \phi_i^*}{\partial x_i} + \partial_i \varphi_i^* - \varrho^*\delta^* - \varrho^* s^* \geq 0, \tag{7.41}$$

which must hold, according to the entropy principle (Postulate 5.3.1) and the δ^*-theorem (Theorem 5.3.1), for all thermodynamic processes.

To exploit the restrictions imposed by this inequality, one can employ the method of Lagrange multipliers proposed by Liu [274], which asserts that, for the case at hand, the following inequality should be valid for arbitrary values of the basic fields (7.16) (cf. (7.6), (7.7), (7.9), (7.11), (7.12) and (7.14))

$$\begin{aligned}
&\varrho^*\dot{\eta}^* + \frac{\partial \phi_i^*}{\partial x_i} + \partial_i \varphi_i^* - \varrho^*\delta^* - \Lambda^{*\varrho}\left(\dot{\varrho}^* + \varrho^*\frac{\partial v_i}{\partial x_i} + \varrho^*\partial_i \mathsf{S}_{ij}^* n_j\right) - \\
&-\Lambda_i^{*v}\left(\varrho^*\dot{v}_i - \frac{\partial \mathsf{t}_{ij}^*}{\partial x_j} - \partial_j \boldsymbol{\tau}_{ij}^* - \varrho^*\kappa_i^*\right) - \Lambda_i^{*s}\left(\varrho^*\mathsf{I}_{ij}^*\dot{s}_j^* - \varrho^*\frac{R^2}{2}\mathsf{S}_{ij}^* n_j n_k \epsilon_{klm}\frac{\partial v_m}{\partial x_l} - \right. \\
&\left. -\frac{\partial \mathsf{m}_{il}^*}{\partial x_l} - \partial_j \boldsymbol{\varpi}_{ij}^* + \epsilon_{ijk}\mathsf{t}_{jk}^* - \varrho^*\nu_i^*\right) - \Lambda^{*e}\left(\varrho^*\dot{e}^* + \frac{\partial q_j^*}{\partial x_j} - \mathsf{t}_{ij}^*\frac{\partial v_i}{\partial x_j} - \right. \\
&\left. -\mathsf{m}_{ij}^*\frac{\partial s_i^*}{\partial x_j} + \partial_j \xi_j^* - \boldsymbol{\varpi}_{ij}^*\partial_j s_i^* - \epsilon_{ijk}s_i^*\mathsf{t}_{jk}^* - \varrho^*\varepsilon^*\right) \geq 0.
\end{aligned} \tag{7.42}$$

Without loss of generality, the balance equations were written here free of external supplies. As usual, it is assumed that the undetermined multipliers $\Lambda^{*\varrho}$, Λ_i^{*v}, Λ_i^{*s} and Λ^{*e} are functions of the same constitutive variables listed in (7.32).

By performing the derivatives presented in (7.42), one obtains an inequality which is explicitly linear in the quantities

$$\frac{\partial v_i}{\partial t},\ \frac{\partial s_i^*}{\partial t},\ \frac{\partial \varrho^*}{\partial t},\ \frac{\partial \beta^*}{\partial t},\ \frac{\partial T}{\partial t},\ \frac{\partial \mathsf{D}_{ij}}{\partial t},\ \frac{\partial s_i^*}{\partial x_j},\ \frac{\partial \varrho^*}{\partial x_i},\ \frac{\partial \beta^*}{\partial x_i},\ \frac{\partial^2 T}{\partial x_i \partial x_j},\ \partial_i \varrho^*,\ \partial_i \beta^*,\ \partial_i \mathsf{H}_{jk}^*.$$

Since the basic fields (7.16) are now arbitrary, so are the above derivatives, and in order to preserve the inequality (7.42) the coefficients of these derivatives must vanish. Consequently,

$$\Lambda_i^{*v} = 0\,, \qquad \Lambda_i^{*s} = \Lambda^{*s} n_i\,, \qquad \mathsf{m}_{ij}^* = 0\,, \tag{7.44}$$

$$\frac{\partial \eta^*}{\partial \varrho^*} - \Lambda^{*e}\frac{\partial e^*}{\partial \varrho^*} = \frac{\Lambda^{*\varrho}}{\varrho^*}\,, \qquad \frac{\partial \eta^*}{\partial \beta^*} - \Lambda^{*e}\frac{\partial e^*}{\partial \beta^*} = 0\,, \tag{7.45}$$

$$\frac{\partial \eta^*}{\partial T} - \Lambda^{*e}\frac{\partial e^*}{\partial T} = 0\,, \qquad \frac{\partial \eta^*}{\partial \mathsf{D}_{ij}} - \Lambda^{*e}\frac{\partial e^*}{\partial \mathsf{D}_{ij}} = 0\,, \tag{7.46}$$

$$\frac{\partial \phi_i^*}{\partial \varrho^*} - \Lambda^{*e}\frac{\partial q_i^*}{\partial \varrho^*} = 0\,, \qquad \frac{\partial \phi_i^*}{\partial \beta^*} - \Lambda^{*e}\frac{\partial q_i^*}{\partial \beta^*} = 0\,, \tag{7.47}$$

$$\frac{\partial \phi_{(i}^*}{\partial T_{,j)}} - \Lambda^{*e}\frac{\partial q_{(i}^*}{\partial T_{,j)}} = 0\,, \qquad \frac{\partial \varphi_i^*}{\partial \varrho^*} - \Lambda^{*e}\frac{\partial \xi_i^*}{\partial \varrho^*} + \Lambda^{*s} n_j \frac{\partial \boldsymbol{\varpi}_{ji}^*}{\partial \varrho^*} = 0\,, \tag{7.48}$$

$$\frac{\partial \varphi_i^*}{\partial \beta^*} - \Lambda^{*e}\frac{\partial \xi_i^*}{\partial \beta^*} + \Lambda^{*s} n_j \frac{\partial \boldsymbol{\varpi}_{ji}^*}{\partial \beta^*} = 0, \tag{7.49}$$

$$\frac{\partial \varphi_i^*}{\partial \mathsf{H}_{jk}^*} - \Lambda^{*e}\frac{\partial \xi_i^*}{\partial \mathsf{H}_{jk}^*} + \Lambda^{*s} n_l \frac{\partial \boldsymbol{\varpi}_{li}^*}{\partial \mathsf{H}_{jk}^*} - \varrho^* \Lambda^{*\varrho}\delta_{i[j} n_{k]} = \frac{\Lambda^{*e}}{2}\epsilon_{jkl}\boldsymbol{\varpi}_{li}^*, \tag{7.50}$$

where the abbreviation $T_{,i} = \partial T/\partial x_i$ was introduced. The remainder of the inequality (7.42) reads

$$\left(\frac{\partial \phi_i^*}{\partial T} - \Lambda^{*e}\frac{\partial q_i^*}{\partial T}\right)\frac{\partial T}{\partial x_i} - \varrho^*\Lambda^{*\varrho}\mathsf{D}_{kk} + \Lambda^{*e}\left(\mathsf{t}_{(ij)}^*\mathsf{D}_{ij} - \mathsf{t}_{[ij]}^*\mathsf{H}_{ij}^* + \varrho^*\varepsilon^*\right) - \varrho^*\delta^* +$$
$$+\varrho^*\left(\hat{\partial}_i\eta^* - \Lambda^{*e}\hat{\partial}_i e^*\right)\mathsf{S}_{ij}^* n_j + \hat{\partial}_i\varphi_i^* - \Lambda^{*e}\hat{\partial}_i\xi_i^* + \Lambda^{*s} n_i\,\hat{\partial}_j\boldsymbol{\varpi}_{ij}^* \geq 0\ , \tag{7.51}$$

with $\hat{\partial}_i \boldsymbol{Q}^* = (\partial_i \boldsymbol{Q}^*)_{\varrho^*,\beta^*,\mathsf{H}_{pq}^*}$ for any given constitutive quantity $\boldsymbol{Q}^*$.

From (7.35) and $(7.48)_1$ immediately follows

$$\phi_{(ij)}^{*I} - \Lambda^{*e} q_{(ij)}^{*I} = 0. \tag{7.52}$$

However, according to (7.35) and (E.2), the appropriate representation of the tensor q_{ij}^{*I} reads

$$q_{ij}^{*I} = -q^{*(1)} n_{<i} n_{j>} - \lambda^* \delta_{ij}, \tag{7.53}$$

where the thermal conductivities $q^{*(1)}$ and λ^* are functions of ϱ^*, β^* and T. Since a representation similar to (7.53) holds also for ϕ_{ij}^{*I}, one concludes that $\phi_{[ij]}^{*I} = q_{[ij]}^{*I} = 0$ and

$$\phi_i^* = \Lambda^{*e} q_i^*\ , \tag{7.54}$$

with $\Lambda^{*e} = \Lambda^{*e}(\varrho^*, \beta^*, T)$.

Condition $(7.47)_1$, combined with (7.53) and (7.54), implies then

$$\lambda^* \frac{\partial \Lambda^{*e}}{\partial \varrho^*} = 0. \tag{7.55}$$

Therefore, excluding the unrealistic solution $\lambda^* = 0$, expression (7.55) constrains Λ^{*e} to $\Lambda^{*e}(\beta^*, T)$. Accomplishing the same procedure with $(7.47)_2$, one finally obtains

$$\Lambda^{*e} = \Lambda^e = \Lambda^e(T). \tag{7.56}$$

On the other hand, $(7.45)_2$ and $(7.46)_2$ combined with (7.56) read

$$\frac{\partial(\eta^* - \Lambda^e e^*)}{\partial \beta^*} = \frac{\partial(\eta^* - \Lambda^e e^*)}{\partial \mathsf{D}_{ij}} = 0, \tag{7.57}$$

and hence, from $(7.46)_1$ and (7.57) ensues the condition

$$\frac{\partial(\eta^* - \Lambda^e e^*)}{\partial T} = -e^*\frac{\partial \Lambda^e}{\partial T}. \tag{7.58}$$

Refusing the possibility that Λ^e be a mere constant, (7.58) implies

$$e^* = e^*(\varrho^*, T), \qquad \eta^* = \eta^*(\varrho^*, T). \tag{7.59}$$

The final step towards the determination of Λ^e arises from the following arguments. First, recall that for the whole "mixture", which is assumed to be a customary polar fluid, there holds the Gibbs equation in its usual form [133, 268], and thereby also the well-known result

$$\frac{\partial(\varrho e)}{\partial T} = T\frac{\partial(\varrho\eta)}{\partial T}. \tag{7.60}$$

On the other hand, relations (6.57) and (6.68) immediately allow one to express (7.60) in the integral form

$$\oint_{\mathcal{S}^2} \frac{\partial(\varrho^* e^*)}{\partial T}\, d^2n = T \oint_{\mathcal{S}^2} \frac{\partial(\varrho^* \eta^*)}{\partial T}\, d^2n. \tag{7.61}$$

Therefore, after multiplication of $(7.46)_1$ by ϱ^* and integration over all orientations, with further subtraction of the result from (7.61), one finally obtains

$$\Lambda^e(T) = \frac{1}{T}, \tag{7.62}$$

provided that $\partial e/\partial T \neq 0$.

Through the introduction of the *partial Helmholtz free energy*

$$\psi^* = e^* - T\eta^*, \tag{7.63}$$

one achieves to ascertain from $(7.45)_1$ one more undetermined multiplier, viz.

$$\Lambda^{*\varrho}(\varrho^*, T) = -\frac{\varrho^*}{T}\frac{\partial\psi^*}{\partial\varrho^*}. \tag{7.64}$$

On the other hand, with the help of (7.37)–(7.39), (7.50), (7.62) and (7.64), it is straightforward to infer that the derivative $\partial\boldsymbol{\varpi}^*_{li}/\partial\mathsf{H}^*_{jk}$ must vanish, independently of the value of Λ^{*s}, in order to satisfy (7.50) for arbitrary values of H^*_{ij}. Consequently, the left hand side of (7.50) becomes a function only of ϱ^*, β^*, T and n_i, implying that

$$\boldsymbol{\varpi}^*_{ij} = \varpi^* \epsilon_{ijk} n_k, \tag{7.65}$$

with $\varpi^* = \varpi^*(\varrho^*, \beta^*, T)$. By inserting (7.62) and (7.65) into $(7.48)_2$ and (7.49) there results

$$\frac{\partial\iota^*_i}{\partial\varrho^*} = \frac{\partial\iota^*_i}{\partial\beta^*} = 0, \tag{7.66}$$

where $\iota^*_i = \varphi^*_i - \xi^*_i/T$. Hence, by considering (7.37) and $(7.38)_1$ there results the representation

$$\iota^*_i = \iota^{(1)}(n_i n_j - \delta_{ij})\mathsf{D}_{<jk>}n_k - \iota^{(2)}\mathsf{H}^*_{ij}n_j, \tag{7.67}$$

where both coefficients $\iota^{(1)}$ and $\iota^{(2)}$ are functions only of the temperature. Finally, (7.50) and (7.64)–(7.67) lead to

$$\varpi^*(\varrho^*, T) = \varrho^{*2}\frac{\partial\psi^*}{\partial\varrho^*} - T\iota^{(2)}. \tag{7.68}$$

This exhausts the consequences of the conditions (7.44)-(7.50). Notice that Λ^{*s} remains undetermined. This is in fact a natural consequence of the constraint (7.7).

7.5 Analysis of thermodynamic equilibrium

The *thermodynamic equilibrium* will be defined here as the state of maximum entropy attained by the medium when it moves in a rigid-body motion, with an uniform temperature field and in absence of internal interactions, i.e.

$$\mathsf{D}_{ij}|_{_E} = \mathsf{H}^*_{ij}|_{_E} = \left.\frac{\partial T}{\partial x_i}\right|_{_E} = \delta^*|_{_E} = \varsigma^*|_{_E} = \kappa^*_i|_{_E} = \nu^*_i|_{_E} = \varepsilon^*|_{_E} = 0, \tag{7.69}$$

where $|_{_E}$ denotes the equilibrium value of the respective quantity.

An immediate consequence of (7.69) is

$$\varepsilon^{*(1)} = 0, \qquad \text{and thence,} \qquad \varepsilon^* = \varepsilon^{*(2)}\mathsf{D}_{kk} + \varepsilon^{*(3)}\mathsf{D}_{<ij>}n_in_j. \tag{7.70}$$

Moreover, from (7.70) and the results obtained in the last section, the inequality (7.51) reduces to

$$\begin{aligned}
\varsigma^{*\mathrm{P}} = {} & \left[3T\iota^{(1)} + \sigma^* + \varrho^*\left(\varepsilon^{*(3)} - T\delta^{*(3)}\right)\right]\mathsf{D}_{<ij>}n_in_j + \\
& + \left[\varrho^{*2}\frac{\partial\psi^*}{\partial\varrho^*} - p^* + \varrho^*\left(\varepsilon^{*(2)} - T\delta^{*(2)}\right)\right]\mathsf{D}_{kk} - \frac{q^{*I}_{ij}}{T}\frac{\partial T}{\partial x_j}\frac{\partial T}{\partial x_i} + \\
& + \sigma^{*I}_{<ij>kl}\mathsf{D}_{kl}\mathsf{D}_{<ij>} + \sigma^{*II}_{<ij>kl}\mathsf{H}^*_{kl}\mathsf{D}_{<ij>} - p^{*I}_{kl}\mathsf{D}_{kl}\mathsf{D}_{ii} + \\
& + 2t^{*(1)}n_i\mathsf{H}^*_{ij}\mathsf{D}_{jk}n_k + 2t^{*(2)}n_i\mathsf{H}^*_{ij}H^*_{jk}n_k + t^{*(3)}H^*_{ij}\mathsf{H}^*_{ij} - \varrho^*T\delta^{*NL} \geq 0,
\end{aligned} \tag{7.71}$$

where the deviation δ^* was decomposed in linear and non-linear parts, viz.,

$$\delta^* = \delta^{*(2)}\mathsf{D}_{kk} + \delta^{*(3)}\mathsf{D}_{<ij>}n_in_j + \delta^{*NL}, \tag{7.72}$$

with $\delta^{*(2)}$ and $\delta^{*(3)}$ being functions only of ϱ^*, β^* and T, while δ^{*NL} is non-linear in D_{ij}, H^*_{ij} and $\partial T/\partial x_i$. Of course, $\delta^{*NL}|_{_E} = 0$ due to (7.69), and the requirement of fore-aft symmetry was already taken into account in (7.70) and (7.72).

An important consequence of the definition of equilibrium stated above is that the inequality (7.71) achieves its minimum value, namely zero, at this state. In other words,

$$\varsigma^{*\mathrm{P}}|_{_E}\left(n_l, \varrho^*, T, \beta^*, \mathsf{H}^*_{mn}, T_{,q}, \mathsf{D}_{rs}\right) = \varsigma^{*\mathrm{P}}\left(n_l, \varrho^*, T, \beta^*, 0, 0, 0\right) = 0. \tag{7.73}$$

Necessary conditions for the occurrence of this minimum follow from the theory of extrema:

$$\left.\frac{\partial\varsigma^{*\mathrm{P}}}{\partial T_{,i}}\right|_{_E} = 0, \qquad \left.\frac{\partial\varsigma^{*\mathrm{P}}}{\partial\mathsf{H}^*_{ij}}\right|_{_E} = 0, \qquad \left.\frac{\partial\varsigma^{*\mathrm{P}}}{\partial\mathsf{D}_{ij}}\right|_{_E} = 0, \tag{7.74}$$

and also the Hessian matrix

$$\left.\frac{\partial^2\varsigma^{*\mathrm{P}}}{\partial\mathcal{X}_A\partial\mathcal{X}_B}\right|_{_E} \quad \text{is positive semi-definite,} \tag{7.75}$$

where $\mathcal{X}_A = \{T_{,i}, \mathsf{H}^*_{jk}, \mathsf{D}_{pq}\}$ and $A = 1, 2, 3, \ldots, 12$. While $(7.74)_{1,2}$ are automatically satisfied, $(7.74)_3$ implies the relations

$$p^* = \varrho^{*2}\frac{\partial \psi^*}{\partial \varrho^*} + \varrho^*\left(\varepsilon^{*(2)} - T\delta^{*(2)}\right), \tag{7.76}$$

$$\sigma^* = -3T\iota^{(1)} - \varrho^*\left(\varepsilon^{*(3)} - T\delta^{*(3)}\right). \tag{7.77}$$

The first of them has a particular significance. Indeed, recalling that $C_i^*|_E = 0$, one immediately concludes from $(6.58)_1$ that

$$p = \oint_{\mathcal{S}^2} p^*\, d^2n, \tag{7.78}$$

with $p(x_i, t)$ denoting the usual thermodynamic pressure. In addition, (6.69) together with (7.36) and (7.70) lead to

$$\oint_{\mathcal{S}^2} \varrho^*\varepsilon^{*(2)}\, \mathrm{d}^2n = 0. \tag{7.79}$$

On the other hand, from (5.12), (5.15) and (7.72) follows

$$\oint_{\mathcal{S}^2} \varrho^*\delta^{*(2)}\, \mathrm{d}^2n = 0. \tag{7.80}$$

The reason for this last result is that the entropy production of the whole "mixture", as given by (5.12), must be a positive semi-definite quadratic form in the (linearized) dissipative variables D_{ij}, H_{ij} and $\partial T/\partial x_i$. A non-vanishing value for the integral (7.80) could thus violate the inequality (5.12), especially for small deviations from equilibrium. Finally, rephrasing the arguments of the last section, once the whole "mixture" is assumed to be a usual polar fluid, for which the Gibbs equation in its customary form applies, there holds the well-known relation

$$p = \varrho^2\frac{\partial \psi}{\partial \varrho}, \tag{7.81}$$

where (due to $(5.9)_1$, (6.88) and (7.63))

$$\psi(x_i, t) = \oint_{\mathcal{S}^2} f^*\psi^*\, \mathrm{d}^2n, \tag{7.82}$$

is the Helmholtz free energy of the "mixture". Notice that the kinetic part of (6.88) was not taken into account in (7.82) since it is non-linear in S_{ij}^*, and therefore, negligible. Gathering the results (7.78)–(7.82) together, one obtains the identity

$$\varrho^2\frac{\partial \psi}{\partial \varrho} = \oint_{\mathcal{S}^2} \varrho^{*2}\frac{\partial \psi^*}{\partial \varrho^*}\, \mathrm{d}^2n, \tag{7.83}$$

which imposes additional restrictions on the form of ψ^*. In particular, (7.83) suggests the introduction of another useful quantity, namely the *chemical potential* $\mu^*(x_i, t, n_j)$, defined by

$$\mu^* = \frac{\partial(\varrho^*\psi^*)}{\partial\varrho^*}, \qquad \text{with} \qquad p + \varrho\psi = \oint_{\mathcal{S}^2} \varrho^*\mu^* \, \mathrm{d}^2 n, \tag{7.84}$$

the last result being inferred from (7.82) and (7.83). Finally, from (7.68), (7.76) and (7.84) one derives the identities

$$\varrho^* \left(\mu^* - \psi^*\right) = p^* - \varrho^* \left(\varepsilon^{*(2)} - T\delta^{*(2)}\right) = \varpi^* + T\iota^{(2)}. \tag{7.85}$$

The residual inequality then reads

$$\begin{aligned} \varsigma^{*\mathrm{P}} = \sigma^{*I}_{<ij>kl}\mathsf{D}_{kl}\mathsf{D}_{<ij>} + \sigma^{*II}_{<ij>kl}\mathsf{H}^*_{kl}\mathsf{D}_{<ij>} - p^{*I}_{kl}\mathsf{D}_{kl}\mathsf{D}_{ii} + 2t^{*(1)}n_i\mathsf{H}^*_{ij}\mathsf{D}_{jk}n_k + \\ + 2t^{*(2)}n_i\mathsf{H}^*_{ij}\mathsf{H}^*_{jk}n_k + t^{*(3)}\mathsf{H}^*_{ij}\mathsf{H}^*_{ij} - \frac{q^{*I}_{ij}}{T}\frac{\partial T}{\partial x_j}\frac{\partial T}{\partial x_i} - \varrho^* T\delta^{*NL} \geq 0. \end{aligned} \tag{7.86}$$

Due to the presence of δ^{*NL}, no further results can be extracted from (7.86) via (7.75). As commented before, this is the price to be paid by the inclusion of the deviation function δ^* in the theory. The analysis of the consequences of (7.75) on (7.86) will be therefore postponed to the particular cases considered in the next section.

7.6 On the microstructure evolution

The results $(7.44)_3$ and (7.65) suffice to rewrite the balance equation of species spin (7.12) as

$$2\mathsf{t}^*_{[ij]}n_j - \varrho^*\epsilon_{ijk}n_j\nu^*_k = \partial_i\varpi^* + \varrho^*\partial_i U^* - \varrho^*\epsilon_{ijk}n_j\left(\mathsf{I}^*_{kl}s^*_l\right)^{\grave{}}, \tag{7.87}$$

where the extrinsic couple c^*_i was related to an external potential $U^*(x_i, t, n_j)$ through the relation $\epsilon_{ijk}n_jc^*_k = \partial_iU^*$. Accordingly, recalling (7.36), (7.40), (7.84), (7.85) and (7.87), one can straightforwardly obtain the transition rate

$$u^*_i = \mathsf{S}^*_{ij}n_j = h^*_i - \frac{D^{*(\mu)}}{\varrho^*}\left[\,\partial_i\left(\mu^* + U^*\right) - \epsilon_{ijk}n_j\left(\mathsf{I}^*_{kl}s^*_l\right)^{\grave{}}\right], \tag{7.88}$$

where

$$h^*_i = \mathsf{W}_{ij}n_j + B^*\left(\mathsf{D}_{ij}n_j - n_j\mathsf{D}_{jk}n_kn_i\right), \tag{7.89}$$

and

$$D^{*(\mu)} = \frac{1}{2}\left(\frac{\nu^{*(1)}}{\varrho^*} + \frac{t^{*(3)} - t^{*(2)}}{\varrho^{*2}}\right)^{-1}, \qquad B^* = D^{*(\mu)}\left(\frac{\nu^{*(2)}}{\varrho^*} + 2\frac{t^{*(1)}}{\varrho^{*2}}\right). \tag{7.90}$$

Moreover, the usual requirement of stability of the isotropic orientational distribution of the suspended molecules at equilibrium implies that $D^{*(\mu)} \geq 0$.

Finally, the insertion of (7.88) into (7.9) leads, with the help of (7.84), to the *microstructure evolution equation*

$$\frac{\partial \varrho^*}{\partial t} = \partial_i \left(D^{*(\varrho)} \partial_i \varrho^* + D^{*(\mu)} \partial_i U^* \right) - \partial_i \left(\varrho^* h_i^* \right) - \frac{\partial}{\partial x_i} \left(\varrho^* v_i \right) - \partial_i \left[D^{*(\mu)} \epsilon_{ijk} n_j \left(I_{kl}^* s_l^* \right)^{\backprime} \right], \quad (7.91)$$

which is, apart from the last term on the right-hand side, an equation of the Fokker–Planck type for the partial density [364], h_i^* and v_i playing the role of drift vectors, while the Fickian diffusion coefficient $D^{*(\varrho)}$ is given by

$$D^{*(\varrho)} = D^{*(\mu)} \frac{\partial^2 \left(\varrho^* \psi^* \right)}{\partial^2 \varrho^*}. \quad (7.92)$$

The similarity between (7.88) and the contemporary generalizations of the empirical law of Fick, as found in the literature on diffusion [115, 315–317, 407], is striking. In particular, the inertial contribution in the last term on the right-hand side of (7.88) is precisely responsible for the hyperbolic features of the evolution equation (7.91), which avoid a rotatory equivalent to the so-called "diffusion paradox" of the classical theory of mixtures, according to which small disturbances in concentration can propagate with infinite speed. By keeping this last term in (7.91), no rotatory diffusion paradox arises. Of course, this small inertial correction manifests itself only in the high-frequency range, tending to be imperceivable in the large time-scales of common rheological processes.

It should be remarked that (7.91) is also valid in the case of non-uniform and time-dependent thermodynamic fields. In fact, it is a continuum generalization of the usual evolution equations utilized in the framework of statistical rheology and molecular theory for dilute and semidilute solutions, as will become clear below. To facilitate the comparison with prior works, the common restriction to incompressible flows will be assumed from now on.

a) (Pseudo) non-ideal solutions. According to the literature on chemical thermodynamics [96, 271, 367], the chemical potential μ^α of the α-th constituent of a mixture can be generally expressed by the formula

$$\mu^\alpha = K^\alpha T \ln \left(f^\alpha \gamma^\alpha \right) + \mu_0, \qquad K^\alpha = \frac{N_\mathrm{A} k_\mathrm{B}}{M^\alpha}, \quad (7.93)$$

where k_B is the Boltzmann constant, N_A the Avogadro number, M^α the molecular weight of the respective constituent, while $f^\alpha = \varrho^\alpha / \varrho$ expresses its mass fraction. In addition, $\mu_0(\varrho, T)$ is a function only of the mixture variables and $\gamma^\alpha(\varrho^\beta, T)$ denotes the so-called *activity coefficient*. If γ^α is just a unit constant, then the behavior of the respective component is said *ideal*, otherwise it is called *non-ideal*. In most common cases, a non-unitary activity coefficient is ultimately related to microscopic interactions among the constituents of the mixture in such a manner that usually only dilute solutions can manifest ideal behavior.

Accepting that the notions just introduced remain valid for the case at hand, the definition (7.93) can be rewritten as

$$\mu^* = KT \ln \left(f^* \gamma^* \right) + \mu_0, \qquad K = \frac{N_\mathrm{A} k_\mathrm{B}}{M}, \quad (7.94)$$

with μ^*, f^*, γ^* and μ_0 having the same meaning of their standard counterparts presented above, while M is related to the molecular weight of the polymer in solution.

Therefore, after neglect of inertial effects by setting $R \to 0$ in (7.13), there follows from (7.19), (7.84), (7.91), (7.92) and (7.94) the evolution equation

$$\frac{\partial f^*}{\partial t} = \partial_i \left(D^{*(\varrho)} \partial_i f^* + \frac{f^* D^*}{KT} \, \partial_i U^* \right) - \partial_i \left(f^* h_i^* \right) - \frac{\partial}{\partial x_i} \left(f^* v_i \right) \ , \tag{7.95}$$

where

$$D^{*(\varrho)} = D^* \left(1 + \frac{\varrho^*}{\gamma^*} \frac{\partial \gamma^*}{\partial \varrho^*} \right), \qquad D^* = D^{*(\mu)} \frac{KT}{\varrho^*}. \tag{7.96}$$

Additionally, according to statistical theories [86, 102, 103], the diffusion coefficient D^* can be defined through

$$D^* = \beta^{*-2} D, \tag{7.97}$$

where $D(\varrho, T)$ is the diffusion coefficient for an isotropic distribution of rods, while the structure parameter β^* is given explicitly by (cf. (7.20) and (7.21))

$$\beta^* \left(x_i, t, n_j \right) = \frac{4}{\pi} \oint_{\mathcal{S}^2} f^* \left(x_r, t, p_s \right) \sqrt{\epsilon_{ijk} \epsilon_{ipq} n_j n_p p_k p_q} \, d^2 p, \tag{7.98}$$

an expression derived from considerations about the topological interactions (*entanglements*) of the rodlike molecules.

Worthy of note is the fact that, due to (7.59), (7.63) and (7.84), the activity coefficient γ^* does not depend on the structure parameter β^*, i.e., it is insensitive to microstructural changes which maintain ϱ^* and T constant. On the other hand, the activity coefficient in semidilute suspensions of rigid rods should be fundamentally related to hydrodynamic as well as entanglement interactions, which hinder the rotatory Brownian motion of the polymer molecules in solution [102, 137]. Once these interactions necessarily depend on the microstructure configuration, it becomes evident that an independence of the activity coefficient on β^* can only occur if γ^* remains always very close to unity (consequently inferring an ideal behavior), except eventually for strongly aligned nematic configurations (e.g., promoted by an intense external field). In other words, a *pseudo non-ideal behavior* of the solution, induced by strong alignment, is allowed. A simple interpretation of this conjecture is afforded by the "mixture" representation: due to the large number of species and the relatively high dilution of the solution, the concentration of each "constituent" tends to remain low sufficient to uphold ideal behavior. Nonetheless, supposing that one of the "constituents" of the suspension achieves an overwhelming concentration, it can eventually exhibit some sensible deviation from ideality, manifested for instance in an abnormal increase of the diffusion coefficient. Notwithstanding, as discussed by Doi & Edwards [102, 103], the experimental corroboration of this hypothesis (e.g., through measurements of birefringence relaxation from the highly ordered state) is hindered by various factors, like chain flexibility, dipole-dipole interactions and other effects.

b) Ideal solutions. In ideal solutions, interactions among the suspended molecules are negligible and the activity coefficient, introduced in (7.94), reduces simply to unity. Evidently, dilute solutions are classical examples of them. Moreover, the absence of microstructural interactions implicates a number of suitable simplifications on the whole theory, since

$$\delta^* = \kappa_i^* = \nu_i^* = \varepsilon^* = 0 \tag{7.99}$$

become valid. Concisely, some of the most important consequences are the reduction of the expressions (7.76), (7.85), (7.90) and (7.96) to

$$p^* = \varrho^{*2} \frac{\partial \psi^*}{\partial \varrho^*} = \varpi^* + T\iota^{(2)} = \varrho^* \left(\mu^* - \psi^*\right) \tag{7.100}$$

and

$$D^{*(\varrho)} = D^{*(\mu)} \frac{KT}{\varrho^*} = \frac{\varrho^* KT}{\zeta^*} = D_0^*, \qquad \zeta^* = 2\left(t^{*(3)} - t^{*(2)}\right). \tag{7.101}$$

The residual inequality (7.86) can now be exploited in the usual manner to get information about the positiveness of some transport coefficients, like the shear viscosity and heat conductivity, in different orientations. In particular, one can find that $\zeta^* \geq 0$. Moreover, according to an old result of Jeffery [231] (see also [56, 347]), the relation

$$B^* = B = \frac{r^2 - 1}{r^2 + 1} \tag{7.102}$$

holds for (semi-)dilute suspensions of non-interacting rigid prolate ellipsoids of aspect ratio $r > 1$, with B being called the *shape factor*.

Hence, restricting attention only to incompressible flows with spatially-independent fields of partial density and negligible inertial effects of the microstructure, one can derive from (7.19), (7.84), (7.91), (7.92), (7.94), (7.100), (7.101) and (7.102) the evolution equation

$$\frac{\partial f^*}{\partial t} = \partial_i \left(D_0^* \partial_i f^* + \frac{f^* D_0^*}{KT} \partial_i U^* \right) - \partial_i \left(f^* h_i^* \right), \tag{7.103}$$

which resembles well the kinetic equation adopted by Doi & Edwards [102] and Dahler et al. [86] for the dynamics of semidilute suspensions of rigid rodlike polymers, provided that the diffusion coefficient D_0^* is (again) given by

$$D_0^* = \beta^{*-2} D_0, \qquad D_0 = D_0(\varrho, T), \tag{7.104}$$

with β^* defined as in (7.98).

A further simplification of (7.101) can also be obtained by assuming

$$\zeta^* = f^* \zeta, \qquad \zeta = \zeta(\varrho, T), \tag{7.105}$$

which seems to be reasonable in the dilute regime. This assumption allows one to rewrite (7.103) as

$$\frac{\partial f^*}{\partial t} = D_0\,\partial_i\left(\partial_i f^* + \frac{f^*}{KT}\,\partial_i U^*\right) - \partial_i\left(f^* h_i^*\right), \tag{7.106}$$

which is readily recognized as the Smoluchowski equation proposed by Kirkwood and co-workers [245, 246, 363] for the rheology of dilute suspensions of rigid rodlike polymers, with the diffusion coefficient obeying the Stokes-Einstein relation

$$D_0 = \frac{\varrho KT}{\zeta}. \tag{7.107}$$

8. Polycrystalline Ice Sheet Dynamics

When the National Geographic Society gave gold medals to Peary and Bartlett, it ignored the black man who had gone farther north than the white sea captain. Like the Eskimos, he was the wrong colour. [...] *This didn't bother the originals. The squat little men who fed John Ross's company in the Gulf of Boothia, who cheerfully extended their hospitality to Parry and Lyon at Repulse Bay and Igloolik, who taught Rae, Hall, and Peary how to exist under polar conditions, gave no thought to such white concepts as fame, ambition, or immortality. These abstract ideas had no meaning; the future to them was no farther away than the next fat seal; beyond that, they did not care to consider its rewards or its terrors. Nor would it concern them for an instant that their names should be left off the maps of the Arctic; after all, they had their own names for the snowy peaks and the frozen inlets that formed their world. It is not their loss that the map ignores them; it is our own.*

Pierre Berton, [39] pp. 630–631

Ice is an abundant mineral. It is a crystalline solid, actually quite brittle. Sometimes it is so hard as to wreck even a huge transatlantic ship. In fact, when its normalized strength is compared with that of other solids, it is found to be among the strongest and hardest [150]. These are uncontestable truths of mankind's quotidian experience. But as taught since long by the atomists, inferences drawn on particular space and time scales might be often treacherous. Chaps. 1 and 2 have expounded how the discrete can turn into a continuum, when the spatial scale is markedly increased; and in Chap. 7 one could learn how Maxwell masterly introduced the concept of time scale in rheology to explain the phenomenon of fluid viscosity as a relaxation process of an elastic behavior. Something qualitatively similar occurs also in the case of ice. Ice sheets are huge ice masses of continental size. Presently there exist only two on the poles, covering Antarctica and Greenland, but there are undisputable evidences for the past existence of other equally large ice sheets covering great parts of North America, Europe and Asia about 100–20 thousand years ago [75, 379]. By the time of maximal volume, these ice sheets might have contained more than three times the actual amount of ice found on Earth. The withdrawal of such a gigantic amount of ice cannot be explained simply by melting – the ice had to have flowed away, like a viscous fluid, towards the ocean. And it continues to flow

Fig. 8.1. Polar ice field in Axel Heiberg Island, Northwestern Canada. By definition, polar glaciers are frozen to their bed, so that ice cannot slide over the bedrock, as in temperate glaciers. The small ice field in this picture flows much as if the ice were a thick molasses poured over the landscape. Aerial photograph made by the Polar Continental Shelf Project of the Canadian Department of Energy, Mines and Resources; published in [353]

from the remaining ice sheets, at a pace of about some to hundreds of meters per year, as detected by measurements and evidenced in aerial photographs like that in Fig. 8.1. Some of the greatest complications to the modeling of ice sheet dynamics are the huge time scales and the relatively high temperatures involved in the process, which together permit a ceaseless changing of the ice microstructure by flow induced anisotropy and recrystallization phenomena. Such microstructural changes may enhance the ice flow up to three fold. In spite of the clear fact that annealing and recrystallization phenomena in ice sheets have their roots in the thermodynamics of polycrystalline media, most approaches neglect this by proposing ad hoc theories which can eventually violate fundamental thermodynamic principles. The objective of this chapter is to present a serious approach to the modeling of induced anisotropy and recrystallization in ice sheets, by using the formalism of mixtures with continuous diversity.

8.1 On *krystallos*... ...or the origins of the science of polycrystalline ice

In the midst of the wide vocabulary of science, there are few particular words which acquired a special, highly distinguished status, by expressing in some peculiar sense the splendid harmony of nature. *Symmetry* and *crystal* are two of them. For thousands of years the meaning of these words has enchanted mankind; the unwearying seeking for their natural causes comprising an essential requisite to anyone really worthy to be called *a man of science*.

Gemstones, the most sumptuous manifestations of the symmetry of crystals, have been symbols of wealth, superstition and power through the generations. Such an allurement can be traced back at least to the 4th millennium B.C., when Bronze Age

settlers began the excavations of turquoise mines near Serabit el-Khadem, in the Sinai Peninsula, some centuries before its domination by the ancient Egyptians [389]. There are also reports of jewels made of lapis lazuli and other semiprecious stones dating from the 3rd millennium B.C., which were found in old Sumerian tombs [187]. Moreover, according to Burke [63] and Greene & Burke [184], archeological investigations indicate that even the prehistoric men of the Paleolithic and early Neolithic Periods collected and admired gemstones like jasper.

One of the first surviving observations of the geometric shapes of minerals – more precisely garnet – is registered in the treatise *Peri teon litheon* (On stones) [28], probably written in the early years of the 3rd century B.C. and ascribed to the Greek philosopher Theophrastos (Theophrastus). Another celebrated exposition about minerals is found in the encyclopedic *Historia naturalis* (Natural history) [435] by the Roman savant Gaius Plinius Secundus (Pliny the Elder), written during the first century of the Christian Era. These two works were so influential during ancient times, that they lasted as foundations of the classification of minerals throughout the Middle Ages.

The human interest on the regular forms of minerals, however, should by no means be underestimated as only of aesthetic, mystic or economic character. Indeed, the term crystal originally derives from the Greek *krystallos*, which simply means. . . ice. This refers to an ancient belief, according to which hyaline quartz, also called rock crystal, was a sort of ice strongly frozen in a permanent rocky state [3, 435]. Such a misconception still persisted during the Middle Ages and the Renaissance – as can be seen for instance in the commentaries of William Gilbert in his *De Magnete* (On the loadstone and magnetic bodies) [159] – being gradually denied only in the course of the 17th century [54, 58]. In fact, as early as 1661 the word crystal was already used in a general sense (instead restricted to hyaline quartz) by Robert Boyle,[1] in his historic *The sceptical chymist* [53].

Ice is not only responsible for the origin of the term crystal. Actually, from the point of view of a glaciologist, it should be stimulating to perceive the outstanding role played by this so common mineral in many historical moments of material sciences. For instance, the first careful study of crystal morphology is attributed to Johannes Kepler, in his *Strena seu de nive sexangula* (A new year's gift or on the six-cornered snowflake) [241] published in 1611. In this short treatise, written in a witty style as a new year's gift to his friend and benefactor Johannes M. Wackher von Wackenfels, Kepler pondered on the reasons of the characteristic hexagonal symmetry of snowflakes. Inspired by other six-fold structures found in nature, like honeycomb cells and pomegranates, he was able to formulate the general fundamen-

[1] Of course, there were earlier also some scarce disclaimers. For example, in 1550 Gerolamo Cardano argued in his book *De subtilitate* (The subtlety of things) [67] that rock crystal should not be a kind of ice, since these two materials react to fire in a completely different way. Similar objections were pointed out by other authors too, as discussed by Adams [3]. Notwithstanding, like some other false concepts of the ancient Greeks which lasted deep-rooted in the medieval culture, the identification of rock crystal as ice came to nought only with the decease of alchemy [13].

tals of cubic and hexagonal packing of spheres[2] (Fig. 8.2). Further, he even managed to speculate that the symmetric morphology of snowflakes could be related to the stacking of minute spherical drops of condensed vapor.

Unfortunately, despite the contiguity of his conjecture to reality, he shortly refused it. This denial was interpreted later as an act intuitively driven by his avoidance from the atomism [365, 431]: "[...] *uno ex atomis Epicuri: verum id nihil est.*[3]" ([241], p. 3).

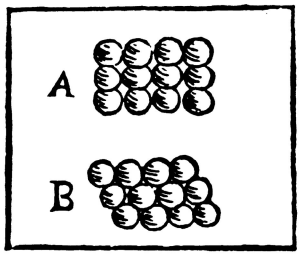


Fig. 8.2. Kepler's drawings of cubic and hexagonal packing of spheres [241]. By attempting to describe the shapes of snowflakes, Kepler choose the less dense structure A.

In *Les météores*, published in 1637 with the *Discours de la méthode* [146], René Descartes adopted also the description of snowflakes as aggregates of small pellets, symmetrically arranged and pressed by strong wind. Some decades later, Robert Hooke performed his pioneering observations on microscope of ice crystals and other materials, collecting them in the memoir *Micrographia* [215], of 1665. Based on his atomistic belief, he extended in this book the concept of densely stacked spheres, in an attempt to describe the geometric shapes of all crystalline substances. At that time, atomistic ideas turned to be fundamentals of a crescent number of crystallographic theories, even despite the strong objections of many prominent scientists. Sympathizers of the corpuscular constitution of crystalline matter included Pierre Gassendi, Robert Boyle, Christiaan Huygens, Niels Steensen (Steno), Isaac Newton and Mikhail V. Lomonosov, among others [13, 63].

An important contribution towards a structured theory of crystals was given at the end of the 18th century by the abbé René-Just Haüy. By extending the ideas of Torbern O. Bergman [35], he presented in a number of essays and monographs (see e.g. [201–203]) the concept of *molécules intégrantes*, i.e., minute polyhedra which should represent the fundamental "building blocks" of crystals. Notwithstanding, Haüy defended insistently until his death in 1822 some erroneous convictions, such as that the *molécules intégrantes* should embody not only the geometrical structure of crystals, but the real molecules of the substance. Despite his efforts to sustain the prestige of his ideas during the turn of the 19th century, noticeable scientific advances – like the reflecting goniometer of William H. Wollaston and the discovery of isomorphism and polymorphism by Eilhardt Mitscherlich (cf. [128, 374]) – led to the inevitable re-examination of Haüy's concepts.

[2]Actually, the origins of the abstract notion of regular packing of corpuscles as the genesis of natural symmetric forms seem to be diffuse and obscure. For instance, a vague reference to the emergence of the hexagonal structure of quartz from a regular stacking of small spheres was given in 1550 by Cardano [67]. There is also a mention by Whyte et al. [431] to some studies of Thomas Harriot at about 1600 concerning the close packing of spherical atoms. In any case, however, it seems clear that Kepler treated this problem in his own individual way, as usual, and doing so he provided the first published evidence of a detailed study on the theme.

[3]Translation: "[...] one of the atoms of Epicurus: but that is really nothing."

Incidentally, both Wollaston and Mitscherlich were adherents of the modern atomic theory proposed in 1808 by John Dalton in *A new system of chemical philosophy* [89]. According to Dalton, the symmetric forms exhibited by crystals should be consequence of some ordered arrangement of the atoms of the various compounds. He admitted, however, that it was premature to propose any detailed description of internal crystalline structures, as long as a better knowledge of the synthesis of chemical substances was not achieved. In order to give a general illustration of his ideas concerning crystal morphology, Dalton chose the example of ice.

He offered an explanation for the anomalous low density of this solid in comparison to cold water and sketched the hexagonal star-like geometry of suddenly congealed ice, as well as its dendritic structure at the beginning of freezing, in terms of the packing of spherical water particles (Fig. 8.3). Curiously, his drafts of the disposition of water molecules in liquid and solid phases seem rather similar to the drawings of stacked spheres presented by Kepler and Hooke more than a hundred years earlier.

It is worthy of notice that the chemical formula assumed by Dalton for the water molecule was HO, instead H_2O. Additionally, by attempting to explain the abnormally low density of ice, he considered that the particles of cold water should accommodate in a dense-packing, while ice should have a less denser "tilted" structure (cf. Fig. 8.3). Nevertheless, such a molecular construction did still not agree quantitatively with the values of density experimentally measured, impelling Dalton to ascribe this discrepancy to the rise of air bubbles in the ice. Despite the apparent consonance of these suppositions with the observed phenomena, it is presently well-known that neither cold water nor ice have the structures conjectured by Dalton.

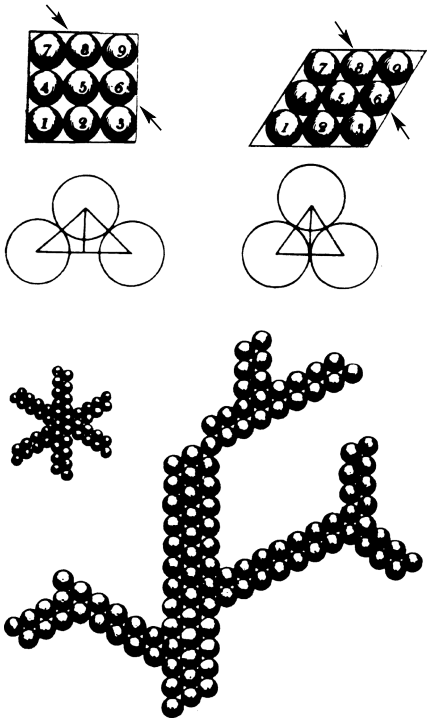


Fig. 8.3. Dalton's sketches of water particles [89]. Top: the arrangements of particles in liquid (left) and solid (right) phases. Middle: cross-sections along the directions indicated by the superposed arrows, showing the vertical packing schemes assumed for liquid water (left) and ice (right); notice that the structure on the left is a dense-packing, while that on the right not. Bottom: structures of suddenly congealed ice (left) and ice at the beginning of freezing (right).

Whatever the case, there remains in this paragraph the example of how far we can go by explaining material behavior based on rather false models.

All these fundamental concepts about crystal morphology promoted a strong impulse to further advances in the physics of crystalline media, culminating with the mathematical theories of space lattices and groups of symmetry by Christian S. Weiss, Friedrich Mohs, Augustin Cauchy, Auguste Bravais, Leonhard Sohncke, Evgraf S. Fedorov, Arthur M. Schoenflies and others (see e.g. [60, 374, 377]). Although the structures of some crystalline chemical compounds were elegantly considered already in the early 19th century by Wollaston [436], many decades were necessary until his work was adequately extended by William Barlow [22–24], who derived space groups by arguing that the arrangement of atoms in the space lattice could be schematically modelled by packings of spheres with distinct colors and sizes, corresponding to different types of constituent particles.

With the emergence of the 20th century, attempts to describe the true internal structure of crystalline media still remained a matter of speculation and controversy, even despite the deeper comprehension of the external morphology and symmetries of crystals, accomplished during 300 years of inquiry. In fact, the solution of this impasse was only determined after the discovery of the phenomenon of X-ray diffraction by crystals, carried out in 1912 by Walter Friedrich and Paul Knipping, under the supervision of Max T. F. von Laue [13, 61]. Just one year later, William H. Bragg and his son, William L. Bragg, elaborated a method of structural analysis of crystals by means of X-ray diffraction and confirmed some of the atomic arrangements predicted many years before by Barlow. Finally, based on earlier experimental results of Friedrich Rinne [362], Ancel St. John [382] and D.M. Dennison [97] concerning X-ray diffraction by ice, W.H. Bragg [55] was able to deduce in 1922 that each oxygen ion of this material should be situated at the center of gravity of its four tetrahedrally arranged nearest neighbors. Consequently, he could explain the hexagonal coordination of oxygen atoms in the crystalline structure of ordinary ice.

Based on these findings, it was easy to conclude that the six-cornered shape of snowflakes was a macroscopic manifestation of the atomic ordering of the ice lattice. The atomism prevailed, and what was once deemed by Kepler as a “Nothing” turned to be recognized as an invaluable “Something”...

8.2 On the freakish nature of polycrystalline ice

Last Section evidenced the role played by ice in the evolution of material sciences and, more particularly, in the establishment of crystallography as a new branch of study. Now it will be shown how this knowledge can be utilized in order to derive conclusions about its material behavior.

Several reasons could be given, either of social, technical or ecological character, to justify man’s interest for ice. There is a particular one, however, which seems to be outstanding before the eyes of most scientists: its unusual – and sometimes perplexing – physical and mechanical properties. For instance, depending on exter-

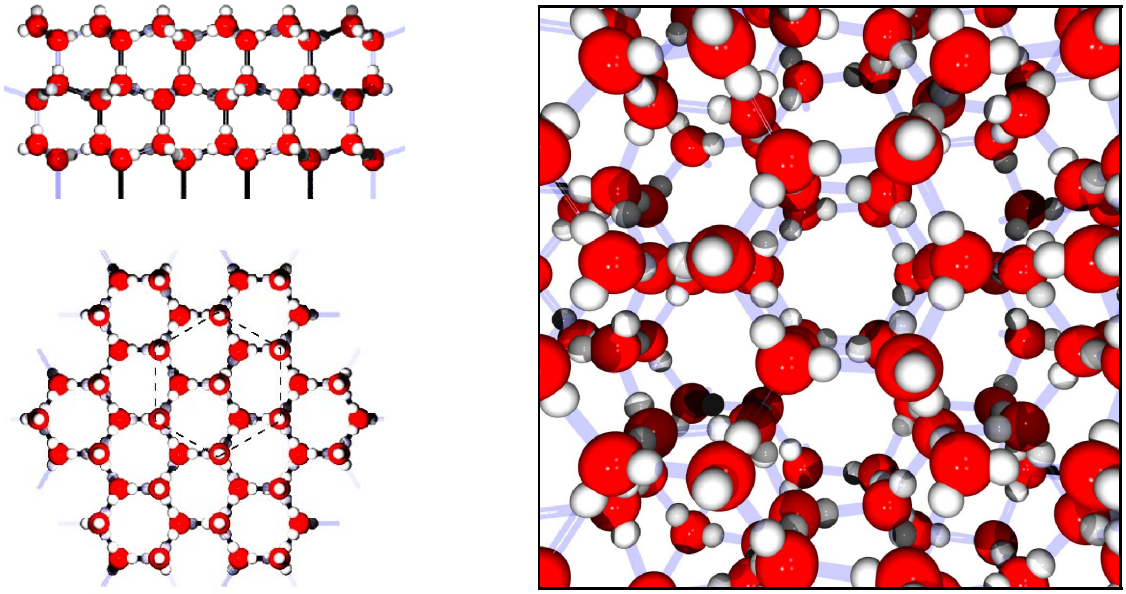


Fig. 8.4. The crystalline lattice of ice *Ih*. Light and dark spheres denote hydrogen and oxygen atoms, respectively, while the tenuous connections define hydrogen bonds. Left: projective view perpendicular to the *c*-axis (top) and along the *c*-axis (bottom); notice the hexagonal cell indicated by dots. Right: perspective view along the *c*-axis. [Courtesy of H. Ehrentraut].

nal factors like temperature and pressure, ice can occur at least in two amorphous forms and nine different crystalline structures (ices *I* to *IX*) [210, 306]. Moreover, the existence of three additional crystalline phases (ices *X* to *XII*) have been a matter of considerable research in the last years [33, 213, 249, 279]. Such a strong polymorphism concedes to water the greatest diversity of solid phases over all known substances.

Under normal atmospheric conditions, water solidifies in the ordinary hexagonal form of ice *I*, usually called ice *Ih* in order to distinguish it from its closely related cubic variant ice *Ic*, which presents a similar tetrahedral coordination of oxygen atoms but arises only at very low temperatures (below -80°C [210]). Ice *Ih* has a rather open lattice, with an atomic packing factor of less than 34% [376] (contrasting with the values of 74% for a close packing of spheres and 68% for a body centered cubic structure) and this accounts for its unexpected low density compared to liquid water. The oxygen ions of the water molecules are disposed in a structure which resembles that of wurtzite or high-tridymite [37, 128, 210, 344, 351]: they are arranged in layers of "puckered" hexagonal rings piled in an alternate sequence of mirror images normal to the optic axis of the crystal, called *c-axis*[4] (Fig. 8.4).

The hydrogen nuclei (protons) remain statistically distributed in the oxygen lattice, building *covalent* as well as *hydrogen bonds* along the lines joining pairs of oxygens. This protonic distribution is however not completely arbitrary: it must conform with the so-called *Bernal-Fowler rules*, which imply that there must be two protons close

[4]Mirror planes and crystallographic axes, as well as other symmetry elements exhibited by the lattice, are fundamental concepts of the space group of ice crystals, playing an important role, e.g., in the interpretation of the patterns observed in diffraction experiments.

to any oxygen, but only one proton per joining line[5]. Hence, each oxygen is involved in two covalent and two hydrogen bonds. The violation of these rules, either by an excess or a deficiency or protons, give rise to particular point defects in the crystalline structure known as *ionization* and *Bjerrum defects*, both essential for the understanding of many peculiar electrical properties of ice [37, 190, 210, 254], as well as its basic micromechanisms of deformation, which will be discussed below. Other point defects, associated with the missing or excess of water molecules, are the *vacancies* and *interstitials*, responsible for the phenomenon of molecular self-diffusion involved in the grain growth of polycrystals, for example. Finally, line and surface defects also occur in the ice lattice, namely *dislocation lines* and *grain boundary surfaces*. As plastic deformation of polycrystalline ice[6] basically involves the motion of these defects through the bulk of material, a brief overview on such micromechanical processes seems to be appropriate.

Monocrystalline ice is a very anisotropic material. Some of its basic features can be well represented by considering a right hexagonal monocrystalline prism, like in Fig. 8.5.

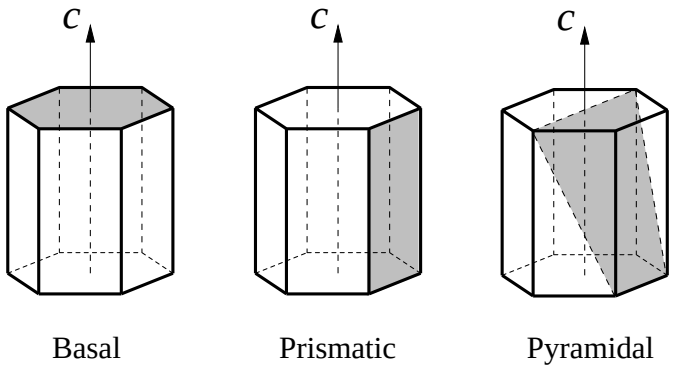


Fig. 8.5. Sketch of a single ice crystal in the form of a right hexagonal prism. Three crystallographic planes are indicated.

Clearly, the basal planes (0001), which are the planes of densest packing of molecules, lie parallel to the layers of oxygen rings already cited, and are therefore orthogonal to the c-axis; the prismatic faces $\{1\bar{1}00\}$ are on the other hand parallel to this axis, while pyramidal planes like $\{1\bar{1}01\}$ cross the bulk of the prism. The relationship between this crystalline symmetry and the microscopic structure of ice is evidenced in Fig. 8.6, and manifests itself either explicitly or implicitly in many natural phenomena, from the growth of snowflakes from vapor [147, 195, 272, 292, 321] to the dynamics of glaciers and ice sheets [170, 210, 342, 369, 402, 413].

Indeed, the fact that single crystals of ice deform very readily when the shear stress has a component acting on the basal plane was recognized since more than

[5]Such a statistical model of the arrangement of hydrogen atoms was first advanced by Pauling [344] in 1935, based on earlier works of Debye [95] and Bernal & Fowler [37]. For more information about ice structure, see for instance the books of Hobbs [210] and Fletcher [141], as well as the detailed microstructural analysis of Nield & Whitworth [323].

[6]From now on, *ice* will refer to the ordinary form of *ice Ih*, since none of its polymorphs will be further considered here.

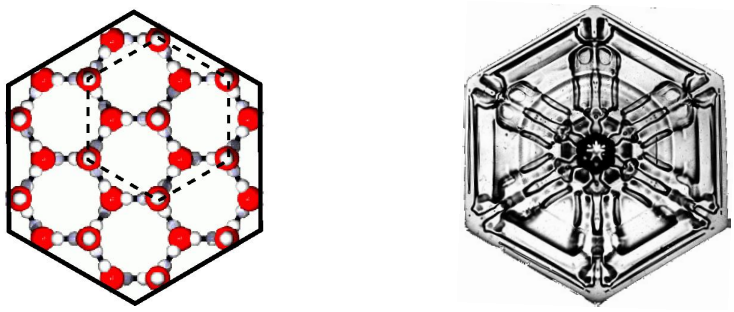


Fig. 8.6. Hexagonal symmetry of ice crystal exhibited in micro- and macroscopic scales. Left: projective view of ice structure (reproduced from Fig. 8.4) evidencing the symmetry in the atomic level. Right: macroscopic manifestation of the hexagonal symmetry in a platelike snowflake [34].

hundred years ago [301], being confirmed in a number of different mechanical tests and field observations [25, 59, 163, 164, 169, 235, 392]. As commented by McConnel [301] after performing his pioneering creep[7] experiments in monocrystalline ice bars:

> "[...] *the crystal behaved as if it consisted of an infinite number of indefinitely thin sheets of paper, normal to the optic axis, attached to each other by some viscous substance which allowed one to slide over the next with great difficulty. This comparison proved to be the key to the whole question of the plasticity of a crystal of ice.*" (p. 325)

The actual explanation for this behavior is that monocrystalline ice at usual temperatures, i.e. above -60°C, deforms mainly by the glide of dislocations on the basal plane, with a direction of propagation (described by the *Burgers vector*) coincident with that of maximum shear stress [152, 163, 235, 239, 278, 420]. Although the precise micromechanisms involved in the motion of such dislocations have been the subject for a considerable amount of work during the last thirty years [113, 150, 162, 163, 210, 276, 351, 422, 430], no complete agreement among the scientists seems to be already achieved. There are nonetheless some favored models; amid them those which assume a process of dislocation slip hindered by drag mechanisms [422], or more particularly, dislocation glide controlled by proton rearrangement [150, 169, 430]. This last process can be resumed as follows. In a hypothetical perfect ice crystal (i.e., without defects), dislocations could move only by generating pairs of Bjerrum defects, as demonstrated by Glen [162]. Due to the large amount of energy necessary to create such defects (0.68 eV per pair, according to Hobbs [210]) the stress required to sustain this process should be exceptionally high, leading eventually to the collapse of the crystalline structure[8] [150, 169]. Hence, there follows that dislocations in a real crystal can only advance when the local configuration of protons is favorable, in the sense that no defects must be created. In other words, the

[7] By *creep* should be understood a plastic or viscous deformation under constant load or stress at relatively high temperatures, the material flowing at its own pace.

[8] A moving dislocation can in principle create also pairs of ionization defects, but since the required energy for production of these defects is even greater, the former situation is more likely to occur, cf. [210, 430].

thermally activated rearrangement of protons is expected to induce the migration of Bjerrum defects which reorient the bonds ahead the dislocations, allowing these line defects to move easily.

Based on this model, it can be shown [9, 169, 422, 429, 430] that the average velocity $\bar{u}$ of dislocations propagating through the stressed ice crystal is proportional to the shear stress τ acting on the glide plane, viz.

$$\bar{u} = \bar{u}_0 \frac{\tau b^3}{k_B T} \exp\left(-\frac{Q}{k_B T}\right) \tag{8.1}$$

where $\bar{u}_0$ is a dimensional constant associated with the kinetics of proton rearrangement, b denotes the length of the Burgers vector, k_B is the Boltzmann constant, T is the absolute temperature and Q represents the activation enthalpy for proton rearrangement glide, i.e., an Arrhenius activation energy for the thermally activated drag mechanism. This expression, combined with the classical Orowan relation for the strain rate [334]

$$\dot{\gamma} = \rho_m b \bar{u} \tag{8.2}$$

and the usual quadratic dependence of the density of mobile dislocations ρ_m on the stress [12] (with $\mu(T)$ denoting the shear modulus)

$$\rho_m = \alpha \left(\frac{\tau}{\mu b}\right)^2 \qquad (\alpha \approx 1), \tag{8.3}$$

leads finally to the creep-rate equation

$$\dot{\gamma} = \frac{\alpha \bar{u}_0}{b} \left(\frac{\tau}{\mu}\right)^n \frac{\mu b^3}{k_B T} \exp\left(-\frac{Q}{k_B T}\right) \tag{8.4}$$

with $n = 3$. According to Weertman [422], the dislocation velocity predicted by (8.1) agrees quite well with experimental data, whereas the

cubic dependence of shear rate on stress seems reasonable (cf. [391]) in view of the wide spread of values found in practice for n, varying (according to him) between 2 and 3.9 for ice single crystals. Moreover, he asserts that the combination of these results with the usual observation of strain softening during transient creep of monocrystalline ice oriented for *easy glide* (i.e., basal slip) gives strong support to accept such a mechanism as a realistic one. Nevertheless, the accuracy of this model should not be overestimated; it is a simplified one. Indeed, most evidences indicate that the best value of n varies with the stress and the duration of the test, being higher at earlier stages of creep and/or larger stresses [163, 210, 392]. This seems to suggest that other mechanisms can possibly be active during the deformation of ice single crystals, although this hypothesis still demands corroboration.

On the other hand, different experimenters have reported creep in single crystals of ice oriented for easy glide with values for the exponent n which are sensibly lower than 3 [113, 114, 163, 210]; most of them about $n = 2$. This led Lliboutry [277] to discard the assumption (8.3) and, instead of it, to suggest that the density of mobile dislocations should be proportional to its production rate. Like Wakahama [420], he

assumed that dislocations in ice would be produced during deformation by means of Frank–Read sources [148] (see also [12]), at a rate proportional to the applied stress. Consequently, invoking again the formulas (8.1) and (8.2), he arrived at an exponent $n = 2$. In passing, it should be noticed that, despite the consideration of Frank–Read sources, Wakahama fitted his experimental curves using $n = 3$.

Whereas the creep of ice single crystals subjected to easy glide appears to be difficult to understand, the situation remains even much more puzzling for polycrystals, as well as single crystals poorly oriented to basal slip, i.e., those compelled to creep by *hard glide* (non-basal slide). Ironically, it was just through the study of the highly intricate behavior of polycrystalline ice that one of the most significant results of contemporary ice mechanics throve: the empiric power law proposed about fifty years ago by Glen [160] and Steinemann [392] to describe the secondary creep of ice polycrystals in uniaxial compression or simple shear, viz.

$$\dot{\varepsilon} = A\,\sigma|\sigma|^{n-1}, \tag{8.5}$$

where $\dot{\varepsilon}$ and σ denote respectively the uniaxial creep rate and stress, while A and n are regarded as constants (in a first approximation, for given isothermal conditions). The experimentally measured values of the exponent n in (8.5) – also named *Glen's flow-law* in the glaciological jargon – range from about 1 to 4, but there is presently a general agreement to use $n = 3$ [343, 412], although Glen [163] suggested that $n = 3.5$ should be more adequate for stresses higher than 1 bar, with its value falling off below this stress level towards about unity. The justification for this suggestion is not merely grounded in experimental data [113], but also in theoretical reasons [143, 218, 219]: a power law function has the well known inconvenience that the viscosity $\eta = d\sigma/d\dot{\varepsilon}$ becomes infinite at vanishing stress, unless when $n = 1$. This shortcoming leads to some interesting consequences, as for example in the modelling of an ice sheet profile: both the surface curvature in the ice divide and the slope at the margin of the ice sheet become infinite [220].

Actually, after observing that relations similar to (8.5) were already utilized in the literature on non-Newtonian fluids since the introduction in 1923 of the power-law equation of de Weale and Ostwald [44, 257, 336] and in metallurgy since the proposition of the concept of power-law creep of solids by Norton [325] in 1929, we conclude that Glen's law was adopted rather belatedly in glaciology. Of course, this does not diminish the usefulness of this equation, which, after appropriate generalizations, has been employed as much in laboratory tests [10, 59, 169] as in the dynamics of glaciers and ice sheets [9, 219, 220, 342, 343, 412, 413], as well as for modelling the creep of ice single crystals either in easy or hard glide [163, 210]. Most of the already cited generalizations are discussed in some detail in the book by Hutter [220], together with the presentation of other possible flow laws and a formal derivation of (8.5) from first principles of continuum mechanics. For the present purposes, however, it suffices to mention only Nye's extension of the Glen law appropriate for multiaxial stresses under non-isothermal conditions, which reads [161, 220, 327, 328, 343, 412]

$$D_{ij} = A' \exp\left(-\frac{Q}{kT}\right) t_{\mathrm{e}}^{n-1} t_{ij} \tag{8.6}$$

where, by assuming the Einstein summation convention of dummy indices,

$$t_{\mathrm{e}}^2 = -II_t = \frac{1}{2}\, t_{ij} t_{ij}, \qquad t_{ij} = t_{ji}, \qquad t_{kk} = D_{kk} = 0. \tag{8.7}$$

In the equations above, t_{ij} and D_{ij} denote the Cartesian components of the tensors of deviatoric (traceless) stress and strain rate, respectively, while A' is a material parameter (dependent on intrinsic properties like impurities, grain size, etc.). Additionally, t_{e} is the so-called effective stress (see e.g. [212, 412]), which is proportional to the square root of the second invariant of the stress tensor, II_t. Eq. (8.6) was first proposed in creep mechanics by Odqvist [331] in 1934.

In the case of pure shear, it can be readily seen that Eq. (8.6) reduces to an expression which well resembles (8.4).[9] This served as motivation to suppose that, at least for temperatures below -10°C, the controlling mechanism of deformation at low stresses in polycrystalline ice should also be basal glide via dislocation sliding [9, 25, 112, 114, 169, 277, 308, 412, 422]. Of course, many objections to this proposition arose [83, 163, 168, 210, 346]. For instance, it has been noticed that the mechanical response of polycrystalline ice exhibits some resemblance with that of single crystals in hard glide: both deform much more slowly than a single crystal in easy glide under otherwise similar conditions (often with strain rates more than 3 orders of magnitude lower [113, 278]); besides that, during the initial transient creep both present strain hardening, in contrast to the strain softening manifested by single crystals in easy glide. The most crucial criticism was, nevertheless, regarding the violation of the *strain compatibility* among neighboring grains [399], which plays an important role in the determination of the shape and orientation of deformed crystals. Yet, inasmuch as we are approaching the domains of the directional properties of polycrystals, it seems appropriate to continue this discussion in the next section, concerned with the emergence of preferred directions, i.e. *textures*, or *fabrics*.[10]

8.3 Modelling induced anisotropy

If an incompressible body suffers uniform strain, in the sense that straight lines are deformed into straight lines, there follows effortlessly from simple geometry that the stretches in five suitable distinct directions suffice to determine the whole deformation of the specimen (actually, these five stretches are just related to the five independent components of the strain tensor [409]).

Based on this simple fact, von Mises [419] derived in 1928 the known result that five independent slip systems[11] are required to impose an arbitrary strain in any crystal which deforms only by glide. Just ten years later, Taylor [399] used von

[9] The careful comparison of (8.4) with (8.6) indicates that the only difference in the form of these two expressions is that the pre-exponential term in the first equation is, a priori, dependent of the temperature, while the parameter A' in the last one is not. Nevertheless, it has been recognized that the assumption that the pre-exponential parameter A' is independent of temperature is in fact not strictly correct [210, 351].

[10] Semantically, these two words have the same meaning. Therefore, they will be used here as synonyms.

[11] A *slip system* is defined by the combination of a crystallographic plane and a particular slip direction on this plane.

Mises' inference to develop his celebrated theory of plastic strain in polycrystalline metals. He assumed that each crystal of the aggregate should suffer exactly the same strain as the bulk (avoiding so the occurrence of microcracks and voids in the material due to incompatibilities among neighboring grains) and on these grounds he calculated deformation and texture development of a polycrystalline medium in terms of its single-crystalline rigid-plastic behavior.

Because of its simplicity, the model proposed by Taylor still continues to be widely used (sometimes with slight modifications) to predict the evolving anisotropy of polycrystals [12, 199, 415]. In spite of that, it is now recognized that the assumptions underlying Taylor's model build just a simplified picture of a commonly much more complex reality. Patchy deformations, grain boundary sliding and migration, shear and kink bands, diffusional flow, polygonization and dynamic recrystallization are just some of the presently known processes which can also occur, allowing inhomogeneous strains [12, 99, 112, 168, 170, 198, 216, 289] and possibly frustrating the requirement of five independent slip systems for each crystal [68, 277, 351, 412].

When applied to ice, Taylor's model presents indeed a very deceptive performance [68, 70, 72]: it demands a contribution to the total strain of about 60% arising from non-basal slip and, consequently, it predicts strain rates which are too low in comparison with experimental data, as well as rather loose fabrics (i.e., low anisotropy). This outcome, added to the lack of experimental evidence on non-basal slip and the observation that hard glide is at least 60 times more difficult to activate than basal easy glide [113, 278], altogether led glaciologists to prefer models which do not strictly require strain compatibility among neighboring grains, with the hope that additional mechanisms (usually not considered in the modelling), like grain boundary migration or polygonization, can fulfil the necessity of coherence in the aggregate. The simplest alternative was obviously to reckon the deformation as produced entirely by basal glide, and assume that the stress, instead strain, is homogeneous in the polycrystal. These two hypotheses, which can be traced back to Sachs [366] and Reuss [361], proved to be considerably more fruitful for the particular case of ice. Indeed, many of the already proposed models for anisotropic ice are based in such premises, even though with some modifications [69, 154, 155, 165–167, 277, 384, 403, 414].

A first effort to describe the fabric evolution of ice under prescribed uniaxial compressive strain was given by Azuma & Higashi [20]. Through direct observation of the crystallographic orientations in thin ice specimens compressed at constant rate, they found that the compressive strain $\varepsilon^g (< 0)$ in each grain was not the same, but correlated with the orientation of its c-axis, ϕ_0, relative to the direction of compression of the sample. Hence, crystals more favorably aligned for deformation by basal glide should exhibit larger strains. The fitting of their data led them to suggest an empirical relation between ε^g and its bulk average, the compressive strain ε, of the form

$$\varepsilon^g = \frac{S}{\bar{S}}\,\varepsilon, \tag{8.8}$$

where $S = \cos\phi_0 \sin\phi_0$ is the *Schmid factor* and $\bar{S}$ its volume average. To compute the rotation of the c-axis of a crystal, they used the simple geometric relation (see

e.g. [375])

$$\sin\phi = (1+\varepsilon^g)\sin\phi_0, \tag{8.9}$$

where ϕ is the angle between the sample's axis of compression and the c-axis, after rotation. This model was extended to the case of uniaxial tension by Fujita et al. [151] and Lipenkov et al. [273], whereas Alley [8] generalized it to pure and simple shear by superposing a sequence of uniaxial strains and rigid-body rotations.

More elaborated approaches, based on the condition that each crystal should undergo the same stress and deform exclusively by basal slip, were proposed by van der Veen & Whillans [414] and Castelnau & Duval [69]. In the first work, a reasonable qualitative agreement of the numeric simulation with laboratory and field observations was occasionally found, but some strong anomalies, as for example the minimum of the strain rate at about 10 % of strain (instead 1 % as observed in practice [59, 228, 236, 237]) evidenced the distinction between simulation and real mechanisms taking place during deformation. Additionally, the similarity of this approach with that of Azuma and Higashi was recognized for simple regimes of deformation. Actually, the greatest merit of the van der Veen-Whillans model lies undoubtedly in their pioneering attempt to simulate dynamic recrystallization in polycrystalline ice, even though only numerically and through artificial criteria: old grains, deformed up to thresholds either of strain or of strain difference (relative to the average deformation of the polycrystal) should be automatically replaced by new ones, undeformed and optimally oriented for basal slip.

In the meanwhile, Azuma [18] attempted to improve his early approach, and presented together with Goto-Azuma [19] an anisotropic generalization of Glen's flow-law (8.6) in the form

$$D_{ij} = A\bar{S}_{(ij)}\left(\bar{S}_{(kl)}t_{kl}\right)^n, \tag{8.10}$$

with

$$A = A'\exp\left(-\frac{Q}{kT}\right), \qquad \bar{S}_{(ij)} = \frac{1}{2}\left(\bar{S}_{ij}+\bar{S}_{ji}\right), \qquad D_{kk} = \bar{S}_{jj} = 0. \tag{8.11}$$

In the equations above, $\bar{S}_{ij}$ denotes the averaged Cartesian components of the *Schmid tensor* $S_{ij} = m_i c_j$, where c_i and m_i are, respectively, unit vectors parallel to the c-axis and to the resolved shear stress in the basal plane, viz.

$$m_i = \frac{T_i}{(T_k T_k)^{\frac{1}{2}}}, \qquad T_i = t_{ij}c_j - (c_k t_{kl} c_l)\, c_i. \tag{8.12}$$

As demonstrated recently by Thorsteinsson et al. [403], the implicit idea of Azuma's model is to replace each crystal of the aggregate by another one, which has the mean orientation given by the averaged Schmid tensor $\bar{S}_{ij}$. Effectively, it can be shown that Sachs' model implies the following flow-law [403]:

$$D_{ij} = A\bar{G}_{ij}, \qquad \text{where} \qquad G_{ij} = S_{(ij)}\left(S_{(kl)}t_{kl}\right)^n. \tag{8.13}$$

Hence, by comparison of (8.10) with (8.13) we conclude that Azuma's flow-law can be directly obtained from Eq. (8.13) through replacing the average of the $(n+1)$-power tensorial product of the symmetric Schmid tensor $S_{(ij)}$ by the $(n+1)$-power tensorial product of its averages; that is, for the case $n = 3$ (say):

$$\overline{S_{(ij)}S_{(kl)}S_{(pq)}S_{(rs)}} \;\Rightarrow\; \bar{S}_{(ij)}\bar{S}_{(kl)}\bar{S}_{(pq)}\bar{S}_{(rs)}. \tag{8.14}$$

Thorsteinsson and his co-workers applied both models (Sachs' and Azuma's) to account for effects of anisotropy in the ice extracted from the Dye 3 borehole, in Greenland. As expected, sensible differences between the two approaches were observed, but the authors could not identify which one had the best performance. They concluded also that no model was able to describe well the strain rate enhancement at Dye 3, and attributed the discrepancies (of $\approx 25\%$) to impurities.

A rather more sophisticated method to describe fabric development in ice was proposed about 5 years ago by Castelnau and co-workers [68, 70–72] through adaptation of the so called *visco-plastic self-consistent* approach (VPSC) developed for metals by Lebensohn and Tomé [262]. In this method, both stress equilibrium and strain compatibility among neighboring grains tend to be satisfied in an approximate manner. Each grain is assumed to be an inclusion embedded in an homogeneous matrix, which ought to represent an averaging of the polycrystalline environment. Hence, neither the stress nor the strain are constrained to be the same for all crystals.

Despite the natural superiority of the VPSC approach in comparison with simpler methods of homogenization of the microstructural behavior, and the usually reasonable agreement of its predictions with experimental observations (see e.g. [71]), some shortcomings still persist. For instance, the method requires the postulation of a constitutive equation for the response of the individual grains, and consequently, appropriate values for all the microscopic parameters involved in this equation must be determined, and in such a way as to provide physically acceptable results at the microscopic as well as the macroscopic levels. In particular, a critical point is the stipulation of the yield shear stress for each slip system. In the case of ice, the best fits of experimental data suggest a resistance to glide in non-basal planes 70 times greater than in the basal plane [68, 71]. Although this sounds tolerable for the case of prismatic slip (as commented before, the observed resistance of ice single crystals to hard glide is more than 60 times higher than for easy glide [113, 278]) the slip activity in pyramidal planes would be inadmissibly high: about 9%. This is rather unphysical, since the occurrence of pyramidal slip in polycrystalline ice is supported neither by theory nor by experiment [94, 214]. The probable reason for this fallacious result is the limited number of deformation mechanisms available in the VPSC: it considers only gliding on crystallographic planes, being therefore incapable, for instance, to treat adequately the details of intergranular interactions as well as recrystallization and intracrystalline processes (kink and deformation bands, polygonization, etc.) which are likely to occur in ice [168, 289, 434].

In order to account for this fault, even more sophisticated (and complex) descriptions of microstructural processes occurring in ice have been recently addressed. For

instance, Meyssonnier & Philip [305] have utilized finite element simulations. In this case, each crystal is treated as a continuum, and complex grain deformations can be simulated without violation of either strain compatibility or stress equilibrium. Due to its complexity, however, only a two-dimensional array with a little more than thousand grains was considered. On the other hand, Ktitarev et al. [252] propose a computer model based on a cellular automaton algorithm to simulate simultaneously grain growth and fabric evolution, including also recrystallization and polygonization processes. This approach has the advantage to be robust and very intuitive, since the polycrystal is regarded as an assemblage of elementary cells, each of them corresponding to a grain of minimum size. Consequently, grains of different sizes can be constructed through aggregation of a larger or smaller number of these cells, which have in common a similar orientation of c-axes. To every cell is associated a crystallographic orientation and an amount of dislocations, in such a way that the microstructural evolution of the medium is based on five rules, related to the increase of dislocation density, crystallographic rotation, grain growth, polygonization and recrystallization. At the present initial stage, however, only a linearized viscous (Newtonian) basal sliding behavior in an one-dimensional array of two thousands of cells (i.e., some hundreds of grains) was considered, since such a detailed description of intracrystalline processes through cellular automata requires vast computer memory and fast processors.

Common to all approaches discussed above is the fact that they constitute discrete models which reckon the polycrystal as an aggregate of a finite number of grains. The advantage of such discrete models is, of course, the potential accuracy of description: each grain of the polycrystal is individually considered. The consequential disadvantage is that they can handle only with small amounts of ice, since the required storage capacity and computational time tend to increase strikingly with the dimensions of the aggregate. In resume: they are definitively not suited for modelling the dynamics of large glaciers and ice sheets. In such cases the best alternative is to resort to a macroscopic continuum description, able to keep somehow the microstructural anisotropy of the medium.

A model of this sort was proposed for instance by Lliboutry [276, 277]. He considered that the stress acting in every crystal was the same, and introduced a dissipation potential for each grain. After a homogenization procedure through averaging of this potential over the whole polycrystalline volume, he was able to obtain an anisotropic flow-law of the polynomial type (see also [220]), which contained a linear dependence on stress, and therefore viscous Newtonian behavior, in addition to the usual cubic dependence of Glen's law. The greater weakness of this theory is that it deals only with a prescribed fabric, being unable to determine its evolution.

Two other approaches to describe the induced anisotropy of ice were proposed five years ago by Meyssonnier & Philip [304] and Svendsen & Hutter [395], through the consideration of a continuous statistical distribution of crystallographic orientations within the polycrystal. The microstructural variable adopted in both works was a typical measure of anisotropy in complex media, namely, an orientational distribution

function (ODF, see e.g. [247]), which gives the fraction of crystals whose c-axes are directed towards a particular orientation in space. Meyssonnier and Philip employed a simpler version of the VPSC model already discussed, by regarding each crystal as a continuous transversely isotropic medium. Instead to treat the polycrystalline body as an aggregate of individual grains, they used the ODF to determine the texture evolution. However, in order to simplify the calculations, only a Newtonian viscous behavior for the grains was considered.[12] On the other hand, Svendsen and Hutter treated ice as a rigid-elastic non-linear creeping material, and utilized the conventional formalism of continuum mechanics [408, 409] to derive the fundamental equations of the model. In particular, they introduced an additional constitutive dependence on a macroscopic tensorial measure of anisotropy: the second momentum of the ODF, named by different authors *alignment, conformation, anisotropy, order* or also *structure tensor* [92, 257]. A common shortcoming of these two theories is that both reckon the polycrystalline ice as a transversely isotropic medium, hence restricting the fabric to remain axially symmetric.

The Svendsen-Hutter theory was first extended in the work of Gödert & Hutter [166] by employing a homogenization technique similar to that used by Lliboutry [277]. Recently, the same authors [165, 167] generalized it further to comprehend also orthotropic symmetry and, motivated by the ideas of the VPSC approach [72], they introduced interactions among neighboring grains. This new version of the theory was implemented numerically in a coupled finite element–finite volume scheme, and comparisons with the GRIP-ice-core data and the predictions of the VPSC model were performed. Curiously, in spite of the fact that Gödert and Hutter employed simply a linear (i.e., Newtonian) viscous relationship between stress and strain rate for basal slip, they showed that their model could fit better the data of GRIP than the non-linear VPSC method.

A purely phenomenological approach to anisotropic ice dynamics, which ignores any micromechanical processes and microscopic interactions at the grain level, was proposed in a series of papers by Morland and Staroszczyk [311, 383, 385–388]. The fundamental idea behind this theory lies in the expectation to obtain a sketchy picture of the anisotropy of the medium from its instantaneous state of deformation. Of course, the supposition of a direct correlation between polycrystalline deformation and fabric is not new, it can be traced back at least to the early model of Azuma & Higashi [20]. The difference is that in the phenomenological approach no compromise with microscopic mechanisms is required. Aiming to maintain the straightforwardness of the Morland–Staroszczyk theory, a significant simplification was assumed by the authors, namely that the evolving anisotropy does not depend on the history of the deformation. In addition, recrystallization processes are included, but through an artificial mechanism [387]: a smooth scaling function, dependent on temperature and the second invariant of strain rate (not strain!), which is unity for low strain rates and falls off above a critical strain rate towards zero, rendering the medium

[12] An even more simplified version of the Meyssonnier-Philip model was recently presented by Gagliardini & Meyssonnier [154, 155] with the aim of a numerical implementation to simulate ice-sheet flow.

isotropic again. The combination of simplicity and flexibility found in this model is in fact its great attractiveness, but also its principal weakness. While it presents itself as a suitable approach to model ice-sheet flow with comparatively low computational costs, it is physically feeble: the microscopic processes occurring within the ice – including changes in grain size and shape, as well as in the fabric itself – are all cryptically subsumed in rheological coefficients, in a similar way as in the case of the pre-exponential coefficient A' of Glen's law (8.6).

8.4 Critique to ad hoc ice sheet models: finding needles in the haystack

After hastily passing throughout the millennial history of the ancients' *krystallos*, as well as the 400 years of modern inquiry in ice, the reader may be asking himself which conclusions could be actually derived from the above discussion. In other words, how large is the present knowledge about the *real* nature of the puzzling mechanical behavior of polycrystalline ice?

To tell the truth, it is still difficult to answer. In earlier times, attempts had been made to apply simple tests (e.g. tensile tests) during some weeks or months to the relatively pure ice made in laboratory, and then to subject the results of these experiments to an elusive mathematical analysis, with further extrapolation of the outcomes to the conditions found in the field. The conflicting conclusions obtained from this methodology have shown that no valuable information can be derived in this way. Indeed the reproduction of the extreme conditions typically found in large glaciers and ice sheets would require tests at quite low stresses (< 0.15 MPa) carried over centuries up to rather large strains (of more than 100%) at temperatures which are simultaneously very high for the material and awfully discomforting for the experimenter (ranging from $-50°$ C to $-0.05°$ C). Under such situations, ice tends to be mechanically very sensitive, in the sense that even little modifications in temperature or stress can be sufficient to change completely the active micromechanisms of deformation and, consequently, the material response.

Deep ice core drilling has been the best alternative during the last 35 years to get round these problems [402]. They offer not only boreholes for closure studies, but also samples of ice slowly deformed during millennia under the right conditions. The interpretation of ice deformation from these data is then performed through a detailed analysis of the ice age, the grain structure and the orientational distribution of the c-axes, i.e. the fabric. Notwithstanding, the relationship between strain history, grain properties and fabric is sometimes not unique, and additional complications are imposed by impurities and the superposition of different mechanical processes along the time. Consequently, it seems that even the combination of laboratory tests, borehole studies and ice core analysis is not sufficient to elucidate the real processes occurring within large ice masses. Something is missing.

Many glaciologists believe (or better saying, hope) that this "missing thing" is just a good computer program for numerical simulation of induced anisotropy and

ice dating, which combined with the conclusions of all other practical methods can define a unique deformation path along the history. This is however, questionable. As asserted by Reeh [360], once sufficient information about ice thickness, upstream histories of accumulation/ablation rates, ice temperature and ice rheology for a given glacier or ice sheet is available, then an accurate dating can in principle be done. However, to know such an "ice rheology" requires the formidable task of determine all the important micromechanical processes which took place in this ice mass during the aging. In fact, the actual comprehension of such micromechanical processes (which include, among other phenomena, induced anisotropy, grain growth and recrystallization) is still rather limited.

Instead of asking what science can tell about the mechanical history of ice, one might turn attention to what the history of science can tell about the mechanics of ice: by borrowing in an abusive way some words of geologists' vocabulary, one could call the last 400 years of ice inquiry the *modern "era" of research*. This "era" can in principle be divided in two main "periods", which will be named here the *morphological "period"* (1611 - 1922) and the *constitutive "period"* (after 1922). During the morphological period, the main attention was given for the geometry and structure of ice crystals, and in particular, snow. It lasted more than 300 years, and finished after a continuous building of knowledge on ice crystallography through the determination of its crystalline structure in 1922. Of course, the research on ice morphology continued forth after this date, but an increasing interest on part of many prominent scientists turned to the mechanical and electrical properties of this material. Actually, somewhat like a "new cycle" of inquiries took place. Nowadays, it could be said that "many needles were already found in the haystack". But there are still many more there to be found, and this is why modern scientists have at present such a wealth of information about ice mechanics, and so few conclusive answers.

Theoretical and numerical work, supported by laboratory tests and borehole/ice-core drillings, are imperative. But presently, major care is necessary in the interpretation of data from theoretical modelling. In the past, great scientists were able to explain a number of observations by using rather fallacious models.

Fig. 8.7. Two aspects of the same structure. Left: detail of the ice lattice, extracted from Fig. 8.4. Right: negative view of the same image, emphasizing the disposition of the empty spaces in a two-dimensional framework.

This is well-illustrated by comparing Fig. 8.7 with Figs. 8.2 and 8.3. A simple model of stacking spheres, as proposed for instance by Dalton, can capture many

morphological features of ice and also explain some particular observations, even in spite of the fact that it is physically misleading.

Therefore, one may answer the question posed at the beginning of this Section with another one: how much of the available theoretical modeling and interpretation of observed data are just false pictures of a completely different reality?

8.5 Fundamental thermomechanics of ice sheets

Generally (see e.g. [220]), the creep of ice sheets and polar glaciers is modeled as the flow of an isotropic, heat-conducting, incompressible and structureless medium, for which there hold the following balance equations of mass, momenta, energy and entropy, respectively,

$$\dot{\varrho} = 0\,, \quad \text{or equivalently} \quad \operatorname{div}\boldsymbol{v} = 0\,, \tag{8.15}$$

$$\varrho\dot{\boldsymbol{v}} - \operatorname{div}\mathbf{t} = \varrho\boldsymbol{g}\,, \tag{8.16}$$

$$\mathbf{t} = \mathbf{t}^{\mathsf{T}}\,, \qquad \text{or equivalently} \qquad \boldsymbol{\vartheta} = \mathbf{0}\,, \tag{8.17}$$

$$\varrho\dot{e} + \operatorname{div}\boldsymbol{q} = \varrho r + \operatorname{tr}\left\{\mathbf{t}\,(\operatorname{grad}\boldsymbol{v})^{\mathsf{T}}\right\}\,, \tag{8.18}$$

$$\varrho\dot{\eta} + \operatorname{div}\boldsymbol{\phi} = \varrho s + \varrho\varsigma\,, \qquad \text{with} \quad \varsigma \geq 0\,, \tag{8.19}$$

where the superposed dot represents the material time derivative, $\boldsymbol{\vartheta}$ is the axial vector of the stress tensor and the superscribed T denotes the transpose of the respective tensor (further details of notation are explained in App. A). The usefulness of (8.15)–(8.19) is actually twofold. On the one hand, (8.15), (8.16) and (8.18) can be used to determine the basic thermodynamic fields of mass density $\varrho(\boldsymbol{x},t)$, translational velocity $\boldsymbol{v}(\boldsymbol{x},t)$ and specific internal energy $e(\boldsymbol{x},t)$ (or alternatively the absolute temperature $T(\boldsymbol{x},t)$, if a thermal equation of state relating both quantities is available) as functions of the position $\boldsymbol{x}$ and time instant t, provided that the external supplies of linear momentum $\boldsymbol{g}(\boldsymbol{x},t)$ and internal energy $r(\boldsymbol{x},t)$ are prescribed, together with constitutive equations for the remaining fields, viz. the Cauchy stress $\mathbf{t}(\boldsymbol{x},t)$, and the heat flux density $\boldsymbol{q}(\boldsymbol{x},t)$. On the other hand, (8.15)–(8.19) can be used instead to derive the explicit forms of such constitutive functions, which are constrained by the second law of thermodynamics through the entropic inequality which emerges from (8.19), after elimination of the specific entropy production $\varsigma(\boldsymbol{x},t)$. This inequality introduces two additional undetermined constitutive quantities, namely the specific entropy $\eta(\boldsymbol{x},t)$ and its flux density $\boldsymbol{\phi}(\boldsymbol{x},t)$, while $s(\boldsymbol{x},t)$ is a prescribed external supply of entropy.

Hence, (8.15)–(8.19) constitute a complete thermodynamic framework for the construction of constitutive theories, from which the celebrated laws of ice sheet modeling, viz. Glen's flow law and Fourier's law of heat conduction, can be derived [220]. Unfortunately, such an approach does not support adequate descriptions of evolving anisotropy and recrystallization phenomena, simply because these processes are essentially of microstructural nature. Notwithstanding, due to the increasing

demand on improvements of Glen's law, anisotropic enhancements have been anyhow proposed during the last 15 years, without much care about thermodynamical first principles. This has given rise to the critical question of whether most of the anisotropic ice sheet models presented so far are indeed portraitures of physical reality or just ingenious casually-coincident mimes of observed data [131].

Owing to this, the aim of this work is to oppose the idiosyncrasy of ad hoc methods, by presenting a completely self-consistent thermodynamic approach for the construction of microstructurally-based constitutive theories for polar ice. The texture (also called fabric[13]) of the material is described by a continuous distribution of c-axes, allowing so the characterization of the most diverse types of anisotropy, while recrystallization processes, like grain growth, polygonization and nucleation, are mainly driven by the density of dislocations. An essential feature of this theory, as in any continuum approach to ice sheet dynamics, is the assumption that every ice sheet "particle" encloses a huge number of grains within a so-called *elementary volume*, located at $\boldsymbol{x}$ (its center of mass). Despite the amount of grains contained in it, such elementary volume is regarded so minute in comparison with the ice-sheet dimensions as to be treated as a "point" of the continuum (for more details, see Chaps. 1 and 2).

8.6 On the continuous diversity of crystallite orientations

The high anisotropy of the viscoplastic response of ice crystals is since long notorious: mechanical tests indicate that, within the range of temperatures found in glaciers and ice sheets, ice single crystals manifest transversal isotropy about their crystallographic axis of symmetry, the so-called *c-axis* [59, 163, 301, 392]. Owing to this, it can be said that, in a polycrystal, ice grains with different c-axis orientations might be regarded – from a thermomechanical point of view – as "distinct materials", even though they are made of the same chemical substance. Following this conjecture, one concludes that the determination of the mechanical response of a large polycrystalline ice mass via homogenization should resemble somewhat the derivation of the properties of a mixture from the respective attributes of its components. Nevertheless, in contrast to usual chemical mixtures, there exists in polycrystalline ice no definite number of "constituents", but rather something like a continuous diversity of possible grain types, or more precisely, lattice orientations.

Evidently, in order to describe the physics of what could be called a "mixture of orientations", some generalization of the classical theory of mixtures is demanded, namely the theory of mixtures with continuous diversity, introduced in Chap. 5 (see also [129, 132]. Succinctly, a mixture with continuous diversity can be regarded as a continuum composed of an infinite number of interacting constituents whose distinctive properties vary *smoothly* from one to another. Mathematically, such a generalization of classical mixture theory can be readily understood by reckoning,

[13] To avoid the vocabulary conflict between geologists and materials scientists, the terms *texture* and *fabric* are used here as synonyms for the preferred orientations of c-axes.

for instance, the constituent field of mass density in an ordinary chemical mixture of N components, viz. $\varrho^{\alpha}(\boldsymbol{x},t)$, with $\alpha = 1,2,\ldots,N$. To derive the respective field for a mixture with continuous diversity we simply allow the species label α

to become a real variable (instead of an integer number) defined in an interval like $[\alpha_{\min},\alpha_{\max}] = \mathcal{A} \subset \mathbb{R}$. The extrema $\alpha_{\min}$ and $\alpha_{\max}$ are so prescribed as to enclose in the interval $\mathcal{A}$ *all* species which can be possibly found in the medium. In this theory, the species label α should have some physical meaning, attributed according to the relevant distinctive property of the species. Moreover, it is straightforward to demonstrate that multiple labels can be introduced (see Chaps. 5 and 6, as well as [129]), usually associated to the components of vector and tensor valued distinctive properties.

In particular, for the case of polycrystalline ice one finds that at least two of those labels are necessary, since any c-axis orientation is uniquely defined in the three-dimensional Euclidean space by its corresponding polar and azimuthal angles, θ and φ, respectively. In principle, we could simply set $\alpha_1 = \theta$ and $\alpha_2 = \varphi$, but calculations using this choice of labels are rather cumbersome. Instead of this, we introduce for convenience a (dimensionless) unit vector $\boldsymbol{n}$, called *orientation vector*, whose spherical coordinates are just θ, φ and $\mathsf{r} = |\boldsymbol{n}| = 1$. It is easy to verify that $\boldsymbol{n}$ is nothing else than the radius vector of the closed, unit spherical surface $\mathcal{S}^2$ embedded in the usual three-dimensional space (see Fig. 6.1). Owing to this, $\mathcal{S}^2$ is referred here as the *orientation space*.

It should be noticed that the new vector valued species label, $\boldsymbol{n}$, has in fact achieved the status of a new field variable, in addition to $\boldsymbol{x}$ and t, in such a way that the "constituent" mass density field in a mixture with continuous diversity reads $\varrho^{*}(\boldsymbol{x},t,\boldsymbol{n})$, where the "$*$" indicates that the respective field is *orientation dependent*, i.e., it is defined, for any instant t, in a 5-dimensional space whose coordinates are $(\boldsymbol{x},\boldsymbol{n})$. Of course, the same procedure can be extended to any other material quantity, enabling so the definition of the orientation dependent fields of translational velocity $\boldsymbol{v}^{*}(\boldsymbol{x},t,\boldsymbol{n})$, Cauchy stress $\mathbf{t}^{*}(\boldsymbol{x},t,\boldsymbol{n})$, specific internal energy $e^{*}(\boldsymbol{x},t,\boldsymbol{n})$, heat flux density $\boldsymbol{q}^{*}(\boldsymbol{x},t,\boldsymbol{n})$, specific entropy $\eta^{*}(\boldsymbol{x},t,\boldsymbol{n})$ and its flux density $\boldsymbol{\phi}^{*}(\boldsymbol{x},t,\boldsymbol{n})$, etc. Furthermore, there is a remarkable characteristic of mixtures with continuous diversity which is not found in usual chemical mixtures; it is called *familiarity*. Generically, two species are said familiar if their distinctive properties (and consequently their physical behavior) are alike, though not identical. Clearly, the concept of familiarity is a direct counterpart of the notion of closeness in the Euclidean space and it is necessary in order to allow treating the orientation $\boldsymbol{n}$ and the position $\boldsymbol{x}$ at the same footing, in a kind of "generalized spatial (Eulerian) description". From this reasoning, it has been shown in Chap. 6 (see also [132]) that the following balance equations of mass, linear and angular momenta, energy and entropy derive from fundamental principles

$$\varrho^{*}_{,t} + \operatorname{div}(\varrho^{*}\boldsymbol{v}^{*}) + \eth\operatorname{iv}(\varrho^{*}\boldsymbol{u}^{*}) = \varrho^{*}\Gamma^{*}\,, \tag{8.20}$$

$$\varrho^{*}\grave{\boldsymbol{v}}^{*} - \operatorname{div}\mathbf{t}^{*} - \eth\operatorname{iv}\boldsymbol{\tau}^{*} = \varrho^{*}\boldsymbol{g}^{*} + \varrho^{*}(\boldsymbol{\kappa}^{*} - \Gamma^{*}\boldsymbol{v}^{*})\,, \tag{8.21}$$

$$\varrho^*\dot{\boldsymbol{\sigma}}^* - \operatorname{div}\mathbf{m}^* - \eth\operatorname{iv}\boldsymbol{\varpi}^* = \varrho^*\boldsymbol{c}^* + 2\,\boldsymbol{\vartheta}^* + \varrho^*(\boldsymbol{\nu}^* - \mathit{\Gamma}^*\boldsymbol{\sigma}^*)\ , \tag{8.22}$$

$$\varrho^*\dot{e}^* + \operatorname{div}\boldsymbol{q}^* + \eth\operatorname{iv}\boldsymbol{\xi}^* = \varrho^* r^* + \operatorname{tr}\boldsymbol{\pi}^* - 2\,\boldsymbol{\vartheta}^*\cdot\boldsymbol{s}^* + \varrho^*(\zeta^* - \mathit{\Gamma}^* e^*)\ , \tag{8.23}$$

$$\varrho^*\dot{\eta}^* + \operatorname{div}\boldsymbol{\phi}^* + \eth\operatorname{iv}\boldsymbol{\varphi}^* = \varrho^* s^* + \varrho^*(\varsigma^* - \mathit{\Gamma}^*\eta^*)\ , \tag{8.24}$$

where the following notation has been introduced (cf. App. A; the symbol $\mathbf{a}^*$ represents any arbitrary tensor field)

$$[\operatorname{gra}\eth\,\mathbf{a}^*]_{ijk} = \frac{\partial \mathsf{a}^*_{ij}}{\partial n_k} - n_k n_l \frac{\partial \mathsf{a}^*_{ij}}{\partial n_l} \;=\; \partial_k \mathsf{a}^*_{ij}\,, \tag{8.25}$$

$$[\eth\operatorname{iv}\,\mathbf{a}^*]_i = [\operatorname{gra}\eth\,\mathbf{a}^*]_{ikk}\ , \tag{8.26}$$

$$[\dot{\mathbf{a}}^*]_{ij} = (\mathsf{a}^*_{ij})_{,t} + v^*_k\,[\operatorname{grad}\mathbf{a}^*]_{ijk} + u^*_k\,[\operatorname{gra}\eth\,\mathbf{a}^*]_{ijk}\ . \tag{8.27}$$

It is worth noticing that, in *spherical coordinates*, the components of the orientational gradient operator (grað) are identical to those of the spatial gradient operator (grad) in two dimensions, i.e. subjected to the constraint $\mathsf{r} = 1$.

From (8.22) and (8.23) one immediately recognizes that ice crystallites are treated here as microstructured media, with $\mathbf{m}^*$ and $\boldsymbol{\sigma}^* = I\boldsymbol{s}^*$ denoting respectively the fields of couple stress and intrinsic angular momentum per unit mass (i.e., specific *c-axis spin*), where $\boldsymbol{s}^*$ denotes the angular velocity of spin (or *c-axis spin velocity*) and I is a material constant, called spin inertia. Moreover, in (8.20)–(8.24) the fields $\boldsymbol{g}^*$, $\boldsymbol{c}^*$, r^* and s^* denote respectively the specific external supplies of momenta, energy and entropy, while $\mathit{\Gamma}^*$, $\boldsymbol{\kappa}^*$, $\boldsymbol{\nu}^*$, ζ^* and ς^* are the specific production terms of mass, momenta, energy and entropy, due to inter-species interactions and dissipative processes. In particular, it is convenient to split the production of energy ζ^* into diffusive (h^*) and non-diffusive (ε^*) parts, viz. $\zeta^* = h^* + \varepsilon^*$. Further, $\boldsymbol{\tau}^*$, $\boldsymbol{\varpi}^*$, $\boldsymbol{\xi}^*$ and $\boldsymbol{\varphi}^*$ are the conductive flux densities of momenta, energy and entropy in the orientation space, due to interactions between *familiar* species (low-angle interactions). Finally, $\boldsymbol{\pi}^*$ represents the specific internal energy production due to the work of stresses, viz.

$$\boldsymbol{\pi}^* = \mathbf{t}^*\,(\operatorname{grad}\boldsymbol{v}^*)^{\mathsf{T}} + \mathbf{m}^*\,(\operatorname{grad}\boldsymbol{s}^*)^{\mathsf{T}} + \boldsymbol{\tau}^*\,(\operatorname{gra}\eth\,\boldsymbol{v}^*)^{\mathsf{T}} + \boldsymbol{\varpi}^*\,(\operatorname{gra}\eth\,\boldsymbol{s}^*)^{\mathsf{T}}\,, \tag{8.28}$$

while $\boldsymbol{u}^*$, called *transition rate*, measures the rate at which matter alters its distinctive properties. For the particular case of polycrystalline ice it has the connotation of a kind of orientational "velocity", describing the rate at which c-axes continuously change their orientations (e.g. by lattice rotation or polygonization). Consequently, the transition rate can be related to the c-axis spin velocity through the relation

$$\boldsymbol{u}^* = \boldsymbol{s}^* \times \boldsymbol{n}\,. \tag{8.29}$$

Eqs. (8.20)–(8.24) constitute the fundamental equations for polycrystalline ice modeled as a mixture with continuous diversity. Notwithstanding, in the present form they are neither sufficient nor adequate to describe fabric (texture) evolution and recrystallization in ice sheets. The justification for this and the derivation of the appropriate balance equations are addressed in the next section.

8.7 Balance equations for polycrystalline polar ice

There exists a marked similarity between (8.20)–(8.24) and the balance equations for chemical mixtures, which arises from the fact that grains in a polycrystal, just as the constituents of a chemically reacting mixture, are strongly interacting open systems. Nevertheless, the contrasting features of both systems are also evident. To understand this, one starts recalling that, in the present description, a single ice sheet particle located at $\boldsymbol{x}$ encompasses in fact a huge number of grains (see Sect. 8.6). In this sense, the point $\boldsymbol{x}$ is *macroscopic*. On the other hand, one observes that there exists just one translational velocity assigned to a given $\boldsymbol{n}$ in this particular point, which implies that $\boldsymbol{v}^*$ actually describes the (instantaneous) *average translational motion* of the crystallites whose c-axes are parallel to $\boldsymbol{n}$, at position $\boldsymbol{x}$. Yet, experience indicates that diffusive motion of grains is not a typical feature found in ice sheets. In other words, crystallites with a particular lattice orientation do not pass through the material, but rather they move with the bulk, even though they do not experience the same deformation as the aggregate. This allows the vanishing of the translational diffusion by setting

$$\boldsymbol{v}^*(\boldsymbol{x}, t, \boldsymbol{n}) = \boldsymbol{v}(\boldsymbol{x}, t)\,. \tag{8.30}$$

It must be emphasized that (8.30) has *no relation at all* with constraints imposed on the crystalline deformation (like the so-called Voigt–Taylor and Sachs–Reuss upper and lower bounds), since the scale considered here is indeed *macroscopic*. This means that strain incompatibilities on the grain level have been already smeared out by homogenization, in such a way that one can consider simply the motion of the ice sheet particles, just as any other macroscopic continuum theory of ice sheets would do. The reason for this is that, in contrast to most models of anisotropic ice, the description of kinematics and microstructure evolution in the present formalism is not based on an averaging of the mechanics of individual crystallites, but rather on the general diffusion theory of structured continua. As a consequence, the results of any microscopically-based homogenization method (as e.g. upper bound or viscoplastic self-consistent approaches [72]) should be compatible, in a large scale, with the relations presented in this work. Whereas the assumption (8.30) could eventually be controversial for a small sample of ice in laboratory, where a material particle contains merely some few grains, for large ice masses like glaciers and ice sheets this seems to be incontestably the most natural choice.

Akin conclusions can be established for the rotational motion of the lattice: since the spin inertia of the c-axes is negligible ($I \to 0$, i.e. crystallographic axes do not continue rotating after stresses are suspended) and the spin velocity $\boldsymbol{s}^*$ is limited, it follows that $\boldsymbol{\sigma}^* = I\boldsymbol{s}^* \to \boldsymbol{0}$. In contrast to (8.30), however, it must be emphasized that the spin velocity $\boldsymbol{s}^*(\boldsymbol{x}, t, \boldsymbol{n})$ generally depends on the orientation $\boldsymbol{n}$. Finally, it is assumed, for simplicity, that $\boldsymbol{g}^* = \boldsymbol{g}$, $\boldsymbol{c}^* = \boldsymbol{0}$, $r^* = r$ and $s^* = s$, reflecting the fact that external body supplies of heat (through solar radiation) and momenta (through gravity) do not produce couples and are effectively independent of the distribution

of c-axes [210]. Hence, from the above arguments one obtains the reduced balance equations for polar ice

$$\dot{\varrho}^* + \eth\mathrm{iv}(\varrho^* \boldsymbol{u}^*) = \varrho^* \Gamma^* , \tag{8.31}$$

$$\varrho^* \dot{\boldsymbol{v}} - \mathrm{div}\, \mathbf{t}^* - \eth\mathrm{iv}\, \boldsymbol{\tau}^* = \varrho^* \boldsymbol{g} + \varrho^* (\boldsymbol{\kappa}^* - \Gamma^* \boldsymbol{v}) , \tag{8.32}$$

$$\boldsymbol{\vartheta}^* = -\tfrac{1}{2} \left(\mathrm{div}\, \mathbf{m}^* + \eth\mathrm{iv}\, \boldsymbol{\varpi}^* + \varrho^* \boldsymbol{\nu}^*\right) , \tag{8.33}$$

$$\varrho^* \dot{e}^* + \mathrm{div}\, \boldsymbol{q}^* + \eth\mathrm{iv}\, \boldsymbol{\xi}^* = \varrho^* r + \mathrm{tr}\, \boldsymbol{\pi}^* - 2\, \boldsymbol{\vartheta}^* \cdot \boldsymbol{s}^* + \varrho^* (\varepsilon^* - \Gamma^* e^*) , \tag{8.34}$$

$$\varrho^* \dot{\eta}^* + \mathrm{div}\, \boldsymbol{\phi}^* + \eth\mathrm{iv}\, \boldsymbol{\varphi}^* = \varrho^* s + \varrho^* (\varsigma^* - \Gamma^* \eta^*) , \tag{8.35}$$

where use was made of (8.15), (A.4) and (8.30). Moreover,

$$\boldsymbol{\pi}^* = \mathbf{t}^* \left(\mathrm{grad}\, \boldsymbol{v}\right)^{\mathsf{T}} + \mathbf{m}^* \left(\mathrm{grad}\, \boldsymbol{s}^*\right)^{\mathsf{T}} + \boldsymbol{\varpi}^* \left(\mathrm{gra}\eth\, \boldsymbol{s}^*\right)^{\mathsf{T}} . \tag{8.36}$$

Further simplifications can still be derived through a suitable constitutive theory (for instance, the vanishing of couple stresses, as will be discussed later). Nevertheless, before approaching the constitutive analysis, it must be recognized that there is still something lacking in the set of equations (8.31)–(8.35). Indeed, while (8.35) expresses thermodynamical irreversibility in a way to be explained later, (8.31)–(8.34) determine the basic fields ϱ^*, $\boldsymbol{v}$, $\boldsymbol{s}^*$ and e^* (or alternatively, temperature) associated to mass exchange, motion, c-axis rotation and thermal processes, respectively. Yet, although recrystallization phenomena are occurring in all these equations (through the mass production Γ^* and other interaction terms), experience demonstrates that no combination of the basic fields mentioned above suffices to describe recrystallization. Hence, one needs an additional balance equation for a new quantity, related to the recrystallization energy. It is known that such an energy is stored from deformation. And it is known that the deformation energy is mainly stored in linear lattice defects; the *dislocations*. Therefore, what is really needed is a balance equation for the dislocation density.

8.8 Dislocation density evolution

In order to derive the balance equation of dislocation from fundamental principles, one must temporarily move to its minute world, the microcrystalline level. A naive sketch of this is given in Fig. 8.8a. Following Kröner [251], one introduces the Burgers vector $\boldsymbol{b}$, characteristic of the dislocation, and a (dimensionless) unit vector $\boldsymbol{l}$, tangential to the dislocation line. With these vectors one builds the diadic $\boldsymbol{l} \otimes \boldsymbol{b}$, called *dislocation tensor*. As discussed by Kröner [250, 251], this tensor completely describes the microscopic state of a dislocation and is closely related to the well-known (macroscopic) dislocation density tensor of classical continuum theories (see [408] and references therein). Therefore, one can use the dislocation tensor to define, through standard methods of homogenization (cf. Chap. 2), the fundamental macroscopic quantities which must appear in the dislocation balance equation.

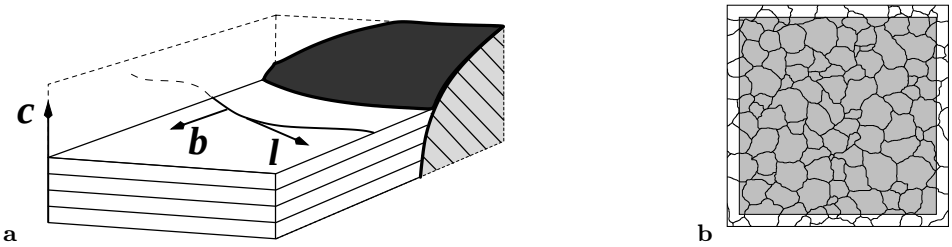


Fig. 8.8. (a) Microscopic volume $\mathcal{V}_\mu$, enclosing a basal dislocation and a grain boundary on its right. (b) Sketch of a volume of size between V_μ and V. The unshaded region near the boundary has a thickness of the order of the dislocation mean free path, λ

Let $\mathcal{V}$ represent the spatial region occupied by an elementary volume of ice (i.e. an ice sheet particle, see Sect. 8.6) located at $\boldsymbol{x}$, containing a huge number of dislocations. It is convenient to assume for a while a static situation in which c-axes do not rotate and no mass flows across the boundaries of $\mathcal{V}$. The Burgers vectors and the tangential unit vectors of the dislocations within $\mathcal{V}$ are respectively described by the distributions $\boldsymbol{b}^*_{\mathsf{D}}(\boldsymbol{x}, t, \boldsymbol{n}; \boldsymbol{r})$ and $\boldsymbol{l}^*_{\mathsf{D}}(\boldsymbol{x}, t, \boldsymbol{n}; \boldsymbol{r})$, where $\boldsymbol{r}$ denotes a position *within the elementary volume*, i.e. on a *microscopic* scale. If $\mathcal{L}$ represents the set of those microscopic points which are instantaneously occupied by dislocations, then it can be easily recognized that

$$(\boldsymbol{b}^*_{\mathsf{D}} \cdot \boldsymbol{b}^*_{\mathsf{D}} \ , \ \boldsymbol{l}^*_{\mathsf{D}} \cdot \boldsymbol{l}^*_{\mathsf{D}}) = \begin{cases} (b^2, \, 1) & \text{if } \ \boldsymbol{r} \in \mathcal{L}, \\ (0 \ , \, 0) & \text{otherwise}, \end{cases} \tag{8.37}$$

where, for simplicity, only one type of Burgers vector has been considered, whose magnitude b is constant. Hence, by dividing the volume V of $\mathcal{V}$ in a great number N of atomic cells of volume b^3, one can introduce through homogenization the orientation dependent *Kröner autocorrelation function*, $k^*_0(\boldsymbol{x}, t, \boldsymbol{n})$, viz. [251]

$$k^*_0 = \frac{1}{Nb^3} \int\limits_{\mathcal{V}} \operatorname{tr} \left\{ (\boldsymbol{l}^*_{\mathsf{D}} \otimes \boldsymbol{b}^*_{\mathsf{D}}) \, (\boldsymbol{l}^*_{\mathsf{D}} \otimes \boldsymbol{b}^*_{\mathsf{D}})^{\mathsf{T}} \right\} \mathrm{d}^3 r = \frac{n^*}{N} b^2 \, , \tag{8.38}$$

where $\mathrm{d}^3 r$ denotes a volume element. In the relation above, (8.37) was used to convert the homogenization integral of (8.38) into a sum over all atomic cells. The quantity $n^*(\boldsymbol{x}, t, \boldsymbol{n})$ defines the instantaneous amount of such cells containing dislocation segments (for given elementary volume and lattice orientation). Now, if $\ell \approx b$ denotes the mean dislocation length within an atomic cell, one can derive, through multiplication of (8.38) by b^{-4}, the identities

$$\frac{k^*_0}{b^4} \approx \frac{k^*_0 \, \ell}{b^5} = \frac{n^* \ell}{Nb^3} = \frac{n^* \ell}{V} = \rho^* \, , \tag{8.39}$$

which define the orientation-dependent *dislocation density* $\rho^*(\boldsymbol{x}, t, \boldsymbol{n})$ as the total length of dislocations (within grains whose c-axes are oriented to $\boldsymbol{n}$) per unit volume. Hence, ρ^* constitutes a new internal variable on the macroscopic scale, related to the microscopic distribution of dislocations through the homogenization integral (8.38).

From the *master balance law* of continuum theory [132, 220, 275] it is known that the time rate of any additive quantity must be balanced by external supplies, internal production, convective and conductive fluxes. For dislocations there are obviously no external supplies and, due to the static situation temporarily assumed here, convective fluxes are absent. Dislocation production (by Frank–Read sources, grain boundary absorption and emission, etc.) is denoted by $\mathit{\Pi}^*$. To compute the conductive flux of dislocations, we adopt the same homogenization method employed above, but now in two steps.

First, one considers the case of a microscopic region $\mathcal{V}_\mu$ like that shown in Fig. 8.8a, whose volume, $V_\mu = N_\mu b^3$, is some *fraction of the mean grain size* (the subscript μ indicates that the value of the respective quantity depends on the size and geometry of the chosen region $\mathcal{V}_\mu$). In this case, the density of dislocations is denoted by ρ^*_μ and, owing to (8.39), it can be easily derived from (8.38) by simply substituting $\mathcal{V}$ and N by $\mathcal{V}_\mu$ and N_μ, respectively. Further, suppose that the (orientation dependent) average propagation velocity of such dislocations is given by $\boldsymbol{U}^*_\mu$. When the dimensions of the region $\mathcal{V}_\mu$ are comparable with the *dislocation mean free path* λ, most dislocations can move through $\mathcal{V}_\mu$ without serious obstructions and the flux density of dislocations is given simply by $\rho^*_\mu \boldsymbol{U}^*_\mu$. This is a conductive flux, because no mass transport is involved with it.

Yet, when the volume of the microscopic region $\mathcal{V}_\mu$ is increased up to the size V of a macroscopic elementary volume $\mathcal{V}$, one concludes from (8.38) and Fig. 8.8b that the conductive flux of dislocations is drastically reduced by a factor proportional to $\lambda \big/ V^{1/3}$. The reason for this lies in the fact that dislocations separated from the boundary of $\mathcal{V}$ by distances larger than λ are usually annihilated or immobilized before having the chance of reaching that boundary. Hence, for sufficiently large elementary volumes, as in the case of a glacier or ice sheet, just the dislocations situated in an infinitesimally thin layer of $\mathcal{V}$ (represented by the unshaded region in Fig. 8.8b) contribute to the conductive dislocation flux density, which consequently becomes *negligible*. Therefore, one concludes that in the absence of matter transport and c-axis rotation, the time rate of the dislocation density is simply balanced by its internal production, i.e., $\rho^*_{,t} = \mathit{\Pi}^*$.

Finally, in a general dynamic situation in which the material in $\mathcal{V}$ moves and rotates arbitrarily, additional convective fluxes of dislocations must be accounted for, due to mass transport, $\rho^* \boldsymbol{v}^*$, and c-axis rotation, $\rho^* \boldsymbol{u}^*$. Consequently, from the above arguments and the master balance law already mentioned, there follows the generic form of the dislocation balance equation

$$\rho^*_{,t} + \operatorname{div}(\rho^* \boldsymbol{v}^*) + \eth\operatorname{iv}(\rho^* \boldsymbol{u}^*) = \mathit{\Pi}^* \,, \tag{8.40}$$

which can be rewritten with the aid of (8.15), (A.4) and (8.30) as

$$\dot{\rho}^* + \eth\operatorname{iv}(\rho^* \boldsymbol{u}^*) = \mathit{\Pi}^* \,. \tag{8.41}$$

Eq. (8.41) is the wanted balance equation of dislocation for polar ice.

8.9 Towards a constitutive theory

What has been presented so far is a continuum approach for the thermodynamics of polycrystalline polar ice involving five orientation dependent basic fields of mass density ϱ^*, translational velocity $\boldsymbol{v}$, c-axis spin velocity $\boldsymbol{s}^*$, internal energy e^* (or alternatively, temperature) and dislocation density $\boldsymbol{\rho}^*$, which can be determined by the balance equations (8.31)–(8.34) and (8.41) provided that constitutive representations for the quantities $\mathit{\Gamma}^*$, $\mathbf{t}^*$, $\boldsymbol{\tau}^*$, $\boldsymbol{\kappa}^*$, $\mathbf{m}^*$, $\boldsymbol{\varpi}^*$, $\boldsymbol{\nu}^*$, $\boldsymbol{q}^*$, $\boldsymbol{\xi}^*$, ε^* and $\mathit{\Pi}^*$ are prescribed. Notwithstanding, such constitutive relations are not arbitrary, since they must satisfy the second law of thermodynamics, which expresses the inherent irreversibility of natural processes through the entropy principle (Postulate 5.3.1) and the *orientation dependent entropy inequality* (5.15) of the Theorem 5.3.1. In fact, insertion of (5.15) into (8.35) yields an entropic inequality with four additional constitutive quantities, namely η^*, $\boldsymbol{\phi}^*$, $\boldsymbol{\varphi}^*$ and the newly introduced *entropy production deviation*, $\delta^*(\boldsymbol{x}, t, \boldsymbol{n})$. This last represents the part of the entropy production due to interspecies interactions, i.e. interactions between crystallites with different c-axis orientations, and can be written as $\delta^* = \varsigma^* - \varsigma^{*\mathrm{P}}$. Evidently, when the material at hand is a single crystal, no deviation exists. Conversely, the vanishing of δ^* in a polycrystal indicates that grains with different lattice orientations behave independently, as isolated systems. In this case, $\varsigma^* = \varsigma^{*\mathrm{P}}$, which is the specific entropy production of an isolated, hypothetical ice single crystal under similar conditions.

Thermodynamically consistent constitutive equations for the quantities already mentioned have been derived through exploitation of the orientation dependent entropy inequality by using standard methods, like e.g. Liu's Lagrange multipliers [275]. Details of such an exploitation are still under analysis and will soon appear elsewhere, but a few relevant issues of it can be already advanced. For instance, it can be shown that the time rate of the dislocation density is an important constitutive variable, which should not be discarded because, among other reasons, it reflects the influence of recovery on the material response. Further, one has obtained that each of the production terms ε^*, δ^* and $\mathit{\Pi}^*$ can be decomposed in two parts, one of them directly proportional to the mass production $\mathit{\Gamma}^*$. Therefore, recrystallization processes involving intercrystalline mass exchanges (e.g. nucleation or grain growth) have inevitable effects upon the energy, entropy and dislocation density of the material. Finally, the most interesting outcome of the constitutive theory at this stage is that the couple stress, $\mathbf{m}^*$, must vanish for ice sheets. Intuitively, this can be readily justified by the fact that couple stresses are generally proportional to gradients of the spin velocity $\boldsymbol{s}^*$ (cf. (8.36)). Yet, experience shows that the spin velocities of c-axes in polar ice are roughly of the same order as the strain rate [229, 238]. Consequently, spin velocity gradients have the magnitude of gradients of strain rate, which are usually neglected in constitutive theories for ice sheets.

The vanishing of couple stresses leads to a curious conclusion concerning the mechanics of polycrystalline ice: whereas the stresses on individual grains are generally non-symmetric (cf. (8.33)), the polycrystalline stress, averaged over all c-axis orientations, is indeed *symmetric*. To demonstrate this, one recalls the homogenization

formulas for all fields occurring in (8.31)–(8.34) and (8.41), which can be obtained as a special case of (6.57), viz.

$$\oint_{\mathcal{S}^2} Y^* \, \mathrm{d}^2 n = Y \,, \qquad \oint_{\mathcal{S}^2} Z^* \, \mathrm{d}^2 n = 0 \,, \tag{8.42}$$
$$Y = \{ \varrho,\ \varrho \boldsymbol{s},\ \varrho e,\ \varrho \eta,\ \mathsf{p} \,;\ \mathbf{t},\ \boldsymbol{q},\ \boldsymbol{\phi} \,;\ \varrho \varsigma,\ \mathit{\Pi} \} \,,$$
$$Z = \{ \varrho \mathit{\Gamma},\ \varrho \boldsymbol{\kappa},\ \varrho \boldsymbol{\nu},\ (\varrho \varepsilon + \varrho \boldsymbol{\nu} \cdot \boldsymbol{s}) \} \,,$$

where $\mathrm{d}^2 n$ denotes an area element on the spherical surface of $\mathcal{S}^2$. If one makes use of (8.42) and the Theorem 6.3.1, which can in this particular case be rewritten in the conditional form

$$\text{if} \ \ \mathbf{a}^*_{ij} n_j = 0 \ \ \forall \, \boldsymbol{n} \in \mathcal{S}^2, \qquad \oint_{\mathcal{S}^2} [\mathring{\partial} \mathrm{iv} \, \mathbf{a}^*]_i \, \mathrm{d}^2 n = 0 \,, \tag{8.43}$$

valid when the arbitrary field $\mathbf{a}^*$ is continuously differentiable in $\mathcal{S}^2$, one can derive, after integration of (8.31)–(8.34) and (8.41) over the whole orientation space, the ordinary balance equations (8.15)–(8.18), together with the habitual dislocation balance equation

$$\dot{\mathsf{p}} = \mathit{\Pi} \ . \tag{8.44}$$

Hence, the view of polycrystalline polar ice as a mixture with continuous diversity has yielded the construction of a thermodynamic continuum approach to ice sheet dynamics, which constitute the first step towards a thermodynamically consistent constitutive theory for large polycrystalline ice masses. In contrast to the fundamentals of other macroscopic models [311, 387], the present theory naturally incorporates recrystallization processes into its balance equations and blends the virtues of an orientational description of the c-axes distribution with the convenience of a macroscopic description.

Compatibility with microscopic models (e.g. [19, 72, 305]) is ensured by the absence of restrictive constraints upon stresses and strains on the crystalline level, while theories based on the concept of an orientation distribution function [154, 166, 395] are also encompassed, in fact with advantages. For instance, it is easy to grasp that, in the present theory, the counterpart of the orientation distribution function (ODF) is the mass fraction $f^* = \varrho^* / \varrho$. Due to (8.42), f^* is *always* a normalized function, even when recrystallization is active, in contrast to the situation found in usual ODF-based theories (cf. [154, 166]).

Concerning recrystallization effects, explicit expressions for the dislocation production $\mathit{\Pi}$ have been recently proposed [2, 188] (for the particular case of ice, see [308]), which can likely be extended to its orientation dependent correlate, $\mathit{\Pi}^*$. The consequences of these expressions for the interaction and production terms occurring in (8.31)–(8.35) are under current analysis, but it seems certain that some concepts from the thermodynamics of continuous reactions [11] should play a fundamental role. For instance, notions akin to that of chemical potential and activity were formerly helpful to clarify the role of interaction terms like $\boldsymbol{\varpi}^*$ and $\boldsymbol{\xi}^*$ [78, 129],

while the latent heat of mass transformation (or better saying, of *recrystallization*) has been recently recognized as an essential concept for linking the productions of energy, ε^*, and entropy, δ^*, to that of mass by recrystallization, Γ^* .

Finally, it should be remarked that mean grain size may appear in the actual description just as a recrystallization parameter, reflecting the assumption that the thermomechanical response of ice should not depend directly on it [59]. Notwithstanding, an extension of the theory, including grain size as an additional distinctive grain property, is straightforward and will be considered in the near future.

9. Glimpsing Further Horizons in a World of Smashing Grains and Melting Icebergs

There is nothing delicate about a glacier. It's a combination of stonecrusher and a gigantic carpenter's plane. It doesn't create enchanted caves around objects of geological interest. It files them down, mashes them to powder, and empties the powder into the Atlantic Ocean.

Peter Høeg (character: Smilla Jaspersen), [211] p. 374

As commented in Chap. 8, ice is among the strongest and hardest materials found in nature. In the bottom of a polar glacier, for instance, it can implacably crush large boulders into pebbles, which eventually yield to gravel and dust. Such destructive processes occur through the phenomena of fragmentation and abrasion of the grains which constitute the bedrock, and have the effect not only of reducing, in a (more or less) gradual way, the mean grain size of the aggregate, but also of changing the character of the grain size distribution. In spite of its evident importance for industrial processing, abrasion and fragmentation of polydisperse granular media have remained virtually untouched in the scientific literature. But some few recent works on this subject (e.g. [242–244]) seem to have shed new light on its relevance. Sect. 9.1 discusses the advantages of considering abrasion and fragmentation phenomena under the perspective of mixtures with continuous diversity. On the other hand, the sand and gravel produced by abrasion and fragmentation on the bedrock of a polar glacier are generally transported by the flowing ice to the margins of the glacier. In particular, when such a glacier ends on the ocean, dirty icebergs may be carved. The amount of terrigenous debris carried by icebergs to deep waters can sometimes be very large, specially during short periods of extremely massive discharge of icebergs, which mark the occurrence of the so called *Heinrich events*. To model the drift of the large ensemble of icebergs supposed to be on the ocean during such events, a continuum approach has recently been proposed by Clarke & La Prairie [77], which curiously has essentially the structure of a theory of mixtures with continuous diversity.

9.1 Isotropic Polydisperse Media: Abrasion and Fragmentation

An interesting application of the theory of mixtures with continuous diversity is on the description of abrasion and fragmentation in polydisperse aggregates of solid spherical grains. For simplicity, one assumes that the medium is dry and all granules are made of the same substance, whose (true) mass density, γ, is constant. In such

a situation, any given grain can be distinguished from the others solely by its size. Therefore it is appropriate to set the species label α (see Chap. 5) equal to μ, where $\mu \in \mathcal{H}$ is any suitable grain size measure (e.g., diameter, volume, surface area, etc.) and $\mathcal{H}$ is its corresponding species assemblage. Clearly, if $\alpha = \mu$, then it immediately follows that $\alpha_{\min} = \mu_{\min}$, $\alpha_{\max} = \mu_{\max}$, and consequently, $\mathcal{H}$ represents simply the range of possible grain sizes in the aggregate.

It should be observed that the choice $\mu_{\min} = 0$ is somewhat captious, although this should be at first sight the most natural assumption, in order to warrant the completeness of the species assemblage. The basic problem is that, in the presence of atmosphere, the premise of a dry medium should fail to hold for the smallest granules: their mass would be so small that hydrodynamic interactions with air could not be neglected. Hence, in order to preserve the completeness of the species assemblage $\mathcal{H}$, one must adopt some additional presupposition. The most trivial options would be either that the granular medium is in vacuum, or that the total mass associated to these minute particles is, for practical purposes, negligible (i.e., the mass loss in the species assemblage is insignificant).

Once the characterization of grain species is defined, one can derive from the results of Chaps. 5 and 6 the balance equations of mass, linear and angular momenta, energy and entropy for the polydisperse media presently considered. Obviously, they correspond to the balance equations for a microstructured medium (6.51)–(6.56) derived in Sect. 6.5.

Hence, at this stage, an interesting issue of the theory is going to be revealed by a short analysis of the balance equation of mass (6.51), which is for commodity rewritten here, viz.

$$\frac{\partial \varrho^*}{\partial t} + \operatorname{div}(\varrho^* \boldsymbol{v}^*) + \frac{\partial}{\partial \mu}(\varrho^* u^*) = \varrho^* \Gamma^* \,. \tag{9.1}$$

Firstly, $\varrho^*(\boldsymbol{x}, t, \mu)$ represents the mass density associated to the grains with size μ. In other words, the mass fraction $f^* = \varrho^*/\varrho$ describes the distribution of grain sizes within the material. Furthermore, from the third term on the left-hand side of (9.1) one concludes that $u^*(\boldsymbol{x}, t, \mu)$ describes a continuous transition of grain sizes, and therefore, it can be interpreted as a measure of abrasion rate (see Fig. 9.1).

This is an important result, for in contrast to former approaches (cf. e.g. [242–244]) abrasion occurs here in a rather different context. Effectively, in usual approaches no explicit connection to any erosional phenomena can be found in the balance equations of mass, momenta and energy, which look more or less like (6.60)–(6.65). This evidently forces one to introduce abrasion by postulating it as a new internal variable, for which an additional evolution equation is required in order to close the system of field equations (the well-known closure problem of continuum mechanics). The crucial point in that ordinary theory is in fact the difficulty in postulating such an evolution equation. For example, if μ were interpreted as a length (say, grain diameter), there would arise arguments in favor of an equation of the so-called Goodman–Cowin type (cf. [242]), which has the structure of a balance equation of momentum, in which u^* plays the role of a velocity. On the other hand, if μ were in-

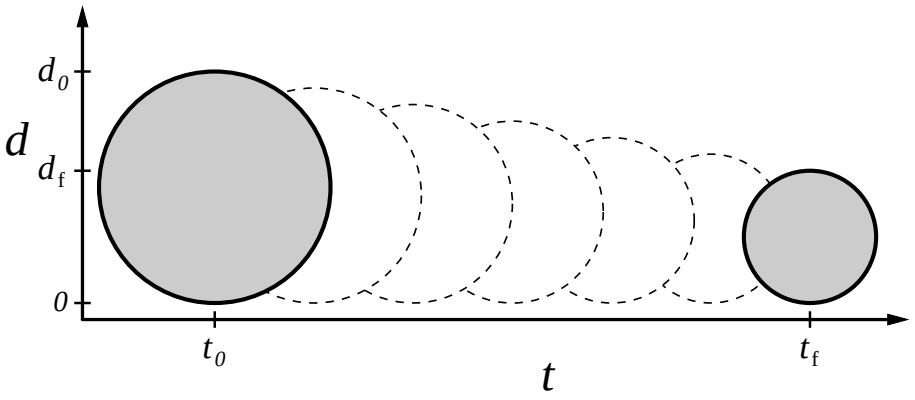


Fig. 9.1. Example of continuous transition through familiar species in a polydisperse granular medium: schematic gradual size reduction in time of a spherical grain, due e.g. to abrasive processes of erosion. The initial and final grain sizes are denoted by $d_0(t_0)$ and $d_\mathrm{f}(t_\mathrm{f})$, respectively, while the transition rate is given in this case by $u^* = \lim_{\Delta t \to 0} \Delta d / \Delta t$.

terpreted as grain volume, we would feel more comfortable in postulating some kind of evolution equation similar to the balance equations of mass, since u^* would be interpreted, in this case, as a kind of volume time rate. Finally, what should prohibit us of reckoning μ as some sort of surface area? Evidently, some information is lacking in the usual approach. Nevertheless, there is no escape: an evolution equation *have to be* postulated.

In the system of balance equations (6.51)–(6.56) utilized here, the situation is quite different. Indeed, erosional effects emerge naturally and we are not forced to introduce any additional internal variable for describing abrasion. Furthermore, the mass production term Γ^* in (9.1) represents also a type of size deterioration which cannot be considered in a usual single-phase continuum theory: it describes mass exchanges between granules of disparate sizes. One can imagine this process as a sudden and dramatic change in grain size, or in other words, *fragmentation*.

Finally, from (6.51)–(6.70) it becomes evident why there is no explicit connection between erosional phenomena and the balance equations of the ordinary continuum theory: both fields u^* and Γ^* leave no vestiges after integration of (9.1) over the whole species assemblage $\mathcal{H}$.

One problem remains, however. Like many other fields present in the balance equations (6.51)–(6.56) (for instance $\mathbf{t}^*$, $\boldsymbol{q}^*$, etc.), the rate of change of grain size u^* must be determined somehow, in order to close the system of equations (again, the "ever-emerging" closure problem of continuum mechanics). Nevertheless, one has now much more freedom, being not obliged to postulate an evolution equation for u^* as in the usual continuum approach. Indeed, fields associated to processes of mass exchange like those described by Γ^* and ϖ^* (for instance, chemical reactions, diffusion, etc.) are most usually described by *constitutive equations*.

Actually, there is a certain physical appeal for adopting constitutive relations for u^* and Γ^*: it is rather intuitive to associate the rates of abrasion and fragmentation to the the strength of contact forces as well as the intensity and frequency of collisions.

In a continuum framework, such events are related to the granular temperature and stretching, which are directly related to the diffusive velocities and the species strain rate of the granular medium. Fortunately, these quantities are precisely fundamental constitutive variables for mixtures with continuous diversity.

In any case, the current approach could in principle also work with an evolution equation for u^*, if preferred. However, by postulating such an equation there would invariably appear additional constitutive terms, and the advantage of using this option on the description level of mixtures with continuous diversity is questionable. Could a theory based on constitutive relations for u^* and Γ^* give better results than a continuum theory with an additional evolution equation for abrasion? It is still too early to answer this question. Recently, Kirchner & Hutter [243] analyzed the performance of continuum models with different evolution equations for abrasion. Their study indicated that an evolution equation of the Goodman–Cowin type is often more robust, having therefore practical advantages. Nevertheless, they recognized that robustness is not a sufficient argument to accept any evolution equation, if no physical justification can be given. In contrast, within the frame of mixtures with continuous diversity, no constitutive theory involving abrasion and fragmentation has been proposed yet.

9.2 Iceberg Ensemble Dynamics

Massive discharges of icebergs seem have occurred at least six times during the last 70.000 years, as registered in the ice-rafted sedimentation in the Labrador Sea [49]. Heinrich [204] was the first to examine such ice-rafting episodes, characterized by sediment layers rich in terrigenous debris and usually poor in planktonic foraminifera. Such deposits record marked decreases in sea surface temperature and salinity, decreases in the flux of foraminifera to the sediments and massive discharge of icebergs originating in eastern Canada. The extreme cooling of surface waters during such events is evidenced by the remarkable distances along which such ice-rafted detrital can be traced: more than 3.000 km. Another very unusual property of Heinrich deposits is the presence of noticeable layers with abundant detrital carbonate – 20% to 25% detrital limestone and dolomite – which constitute a composition markedly distinct from that in the ambient glacial sediment, which consists mostly of quartz and feldspar, variable amounts of black volcanic glass and only a few per cent detrital carbonate. This serves as evidence for the sources of the icebergs, since dolomite and limestone bedrock is found in Hudson Strait.

The model of Clarke & La Prairie [77] for the dynamics of an ensemble of icebergs is based on the concept of a spatially-averaged smooth field to describe iceberg volume per unit area of ocean surface. This field has dimension of length, and consequently is called the *effective thickness field* $h^*(\boldsymbol{x}, t, s)$, where s denotes some particular size parameter as volume, cross-sectional area at the water line or water line perimeter. The iceberg volume within an area A is in any case given by

$$V(t) = \int_S \int_s h^*(\boldsymbol{x}, t, s) \mathrm{d}s \mathrm{d}S \,, \tag{9.2}$$

and from this relation they were able to derive an iceberg volume balance equation of the form

$$\frac{\partial h^*}{\partial t} + \mathrm{div}\,(h^* \boldsymbol{v}^*) + \frac{\partial}{\partial s}\,(h^* u^*) = h^* \Gamma^* - \mathrm{div}\boldsymbol{J} \,, \tag{9.3}$$

where $\boldsymbol{J}$ is an additional stochastic diffusion term to account for the effects of further details of the iceberg geometry which can affect the drift of the icebergs.

The similarity of this description with the basic structure of the theory of mixtures with continuous diversity is striking. The combination of these two approaches for the description of Heinrich events is under progress.

Appendices & Back Matter

Appendices

A Some remarks about notation

All fields are assumed to be continuously differentiable functions of their variables, except when specific singular features are explicitly mentioned.

An Euclidean space of dimension n is denoted by $\mathbb{R}^n$. In particular, any point in a three-dimensional Euclidean space is defined in a Cartesian coordinate system by the components of the *position vector* $x_i \in \mathbb{R}^3$, with $i = 1, 2, 3$. For brevity, when using component notation, x_i will often be referred as "the position" instead of the more accurate name "the Cartesian components of the position vector". The same holds for all other vectors and tensors.

Scalar, vector and tensor valued fields are represented by Greek and Latin letters. In particular, *scalars are written in lightface, vectors in slanted or italic boldface, and tensors in upright boldface.* Components of vectors and tensors are expressed in Cartesian indicial notation using *italic Latin indices* ($i = 1, 2, 3$), together with the usual summation convention of repeated indices. For instance, some frequently used definitions are ($\boldsymbol{a}$, $\boldsymbol{A}$, $\mathbf{a}$, $\mathbf{A}$, denote arbitrary vectors and tensors, respectively)

$$\boldsymbol{a}\cdot\boldsymbol{A} = a_i A_i\,, \quad [\boldsymbol{a}\otimes\boldsymbol{A}]_{ij} = a_i A_j\,, \quad [\mathbf{a}\mathbf{A}]_{ij} = \mathsf{a}_{ik}\mathsf{A}_{kj}\,, \tag{A.1}$$

$$[\boldsymbol{a}\times\boldsymbol{A}]_i = \epsilon_{ijk} a_j A_k\,, \quad \operatorname{tr}(\mathbf{a}) = \mathsf{a}_{ii}\,, \quad \mathbf{A}_{,t} = \frac{\partial \mathbf{A}}{\partial t}\,, \tag{A.2}$$

$$[\operatorname{grad}\mathbf{A}]_{ijk} = \frac{\partial \mathsf{A}_{ij}}{\partial x_k}\,, \qquad [\operatorname{div}\mathbf{a}]_i = [\operatorname{grad}\mathbf{a}]_{ikk}\,, \tag{A.3}$$

$$[\dot{\mathbf{a}}]_{ij} = (\mathsf{a}_{ij})_{,t} + v_k\,[\operatorname{grad}\mathbf{a}]_{ijk}\,, \quad \vartheta_i = \tfrac{1}{2}\epsilon_{ijk}\mathsf{t}_{kj}\,, \tag{A.4}$$

where ϵ_{ijk} and ϑ_i represent the components of the permutation tensor and of the axial vector of stress.

Submanifolds of $\mathbb{R}^n$ are indicated by calligraphic letters ($\mathcal{A}$, $\mathcal{B}$, etc.). For instance, one defines the material body as $\mathcal{B} \subset \mathbb{R}^3$, while any time instant is given by $t \in \mathcal{T} \subseteq \mathbb{R}^1$. Of course, the configuration of $\mathcal{B}$ in $\mathbb{R}^3$ is a function of t [290]. Another submanifold of particular interest is the (2-)sphere $\mathcal{S}^2 \subset \mathbb{R}^3$, which is envisaged as a closed spherical surface of unit radius embedded in $\mathbb{R}^3$ [1]. Any point of $\mathcal{S}^2$ can in principle be identified by two ways, namely the spherical (polar and azimuthal) angles θ and φ, or the two independent Cartesian components of the normalized *orientation vector* $n_i \in \mathbb{R}^3$ (with $n_i n_i = 1$), which is nothing else than the unit radius vector of the spherical surface of $\mathcal{S}^2$ in $\mathbb{R}^3$.

Cartesian components of the gradient and divergence operators in $\mathbb{R}^3$ and $\mathcal{S}^2$ are given respectively by (Q, $\boldsymbol{Q}$ and $\mathbf{Q}$ denote arbitrary scalar, vector and tensor valued fields)

$$(\mathrm{grad} Q)_i = \frac{\partial Q}{\partial x_i}\,, \qquad (\mathrm{gra}\eth\, Q)_i = \frac{\partial Q}{\partial n_i} - n_i n_j \frac{\partial Q}{\partial n_j} = \partial_i Q\,, \tag{A.5}$$

$$\mathrm{div}\boldsymbol{Q} = \frac{\partial Q_i}{\partial x_i}\,, \qquad \eth\mathrm{iv}\boldsymbol{Q} = \frac{\partial Q_i}{\partial n_i} - n_i n_j \frac{\partial Q_i}{\partial n_j} = \partial_i Q_i\,, \tag{A.6}$$

$$(\mathrm{div}\,\mathbf{Q})_i = \frac{\partial \mathsf{Q}_{ij}}{\partial x_j}\,, \qquad (\eth\mathrm{iv}\,\mathbf{Q})_i = \frac{\partial \mathsf{Q}_{ij}}{\partial n_j} - n_j n_k \frac{\partial \mathsf{Q}_{ij}}{\partial n_k} = \partial_j \mathsf{Q}_{ij}\,. \tag{A.7}$$

In particular, the operators gra$\eth$ and $\eth$iv are sometimes also called *orientational gradient and divergence operators*[1].

Surface and volume differentials in $\mathbb{R}^3$ are denoted by d^2x and d^3x, whereas line and surface differentials on $\mathcal{S}^2$ by $\mathrm{d}n$ and d^2n, respectively. Consequently, an integral in a product space like $\mathcal{B}\times\mathcal{S}^2$ (say) can be written as

$$\int\limits_{\mathcal{B}\times\mathcal{S}^2} (\dots)\,\mathrm{d}^2n\,\mathrm{d}^3x \;=\; \int\limits_{\mathcal{B}} \left\{ \oint\limits_{\mathcal{S}^2} (\dots)\,\mathrm{d}^2n \right\} \mathrm{d}^3x \;=\; \oint\limits_{\mathcal{S}^2} \left\{ \int\limits_{\mathcal{B}} (\dots)\,\mathrm{d}^3x \right\} \mathrm{d}^2n, \tag{A.8}$$

where the circle in one of the integral symbols emphasizes the integration over a closed region (in this case, a closed surface).

Finally, avant-garde letters ($\mathcal{A}$, $\mathbf{b}$, etc.) are used in reference to generic quantities and fields.

B On frame changes

Invariance of thermodynamic fields and their balance equations with respect to arbitrary changes of observer (i.e. reference frame) is mainly analysed in Chap. 4. Owing to this, the choice of the fields considered in this Appendix is in principle inspired by the subject of that Chapter (viz. a reactive mixture of N anisotropic fluids with directors d_i^α ($\alpha = 1, 2, \dots, N$)) but the generality of the current discussion is not constrained to the frames of Chap. 4 at all: the formulas presented below are valid in any situation and further transformation rules for other fields can be easily derived using the same arguments and procedures demonstrated here.

Succinctly, *Euclidean transformations* represent general changes of reference frame which preserve distances and time intervals. Accordingly, the position x_i and time instant t measured in an arbitrary frame of reference can be related to the respective quantities $(x_i)_{\text{IO}}$ and $(t)_{\text{IO}}$ seen by an inertial observer (IO) through the Euclidian transformation [275, 317]

$$x_i = \mathsf{O}_{ij}\,(x_j)_{\text{IO}} + b_i\,, \qquad t = (t)_{\text{IO}} + a\,, \tag{B.1}$$

[1] In some works (e.g. [78]) the orientational gradient operator is defined in a slightly different form, viz. $\epsilon_{ijk} n_j\, \partial/\partial n_k$.

where the time dependent orthogonal tensor $\mathsf{O}_{ij}(t)$ (with $\mathsf{O}_{ik}\mathsf{O}_{jk} = \delta_{ij}$) denotes a proper transformation[2] (i.e., a rotation), $b_i(t)$ represents the relative position of both frames and a is a time shift. From (B.1), the following transformation rules can be derived [82, 266, 275, 317] (notice that the director d_i^α transforms like a displacement):

$$v_i = \mathsf{O}_{ij}\,(v_j)_{\text{IO}} + \Omega_{ij}\,(x_j - b_j) + \dot{b}_i\ , \qquad \frac{\partial v_i}{\partial x_j} = \mathsf{O}_{ik}\mathsf{O}_{jl}\left(\frac{\partial v_k}{\partial x_l}\right)_{\text{IO}} + \Omega_{ij}\ , \tag{B.2}$$

$$\dot{v}_i = \mathsf{O}_{ij}\,(\dot{v}_j)_{\text{IO}} + \ddot{b}_i + \dot{\Omega}_{ij}\,(x_j - b_j) - \Omega_{ik}\Omega_{kj}\,(x_j - b_j) + 2\Omega_{ij}\left(v_j - \dot{b}_j\right)\ , \tag{B.3}$$

$$d^\alpha = (d^\alpha)_{\text{IO}}\ , \qquad d_i^\alpha = \mathsf{O}_{ij}\left(d_j^\alpha\right)_{\text{IO}}\ , \qquad \frac{\partial d_i^\alpha}{\partial x_j} = \mathsf{O}_{ik}\mathsf{O}_{jl}\left(\frac{\partial d_k^\alpha}{\partial x_l}\right)_{\text{IO}}\ , \tag{B.4}$$

$$\dot{d}_i^\alpha = \mathsf{O}_{ij}\left(\dot{d}_j^\alpha\right)_{\text{IO}} + \Omega_{ij}d_j^\alpha\ , \qquad \frac{\partial \dot{d}_i^\alpha}{\partial x_j} = \mathsf{O}_{ik}\mathsf{O}_{jl}\left(\frac{\partial \dot{d}_k^\alpha}{\partial x_l}\right)_{\text{IO}} + \Omega_{ik}\frac{\partial d_k^\alpha}{\partial x_j}\ , \tag{B.5}$$

$$\ddot{d}_i^\alpha = \mathsf{O}_{ij}\left(\ddot{d}_j^\alpha\right)_{\text{IO}} + \dot{\Omega}_{ij}d_j^\alpha - \Omega_{ik}\Omega_{kj}d_j^\alpha + 2\Omega_{ij}\dot{d}_j^\alpha\ , \tag{B.6}$$

with $\Omega_{ij} = \dot{\mathsf{O}}_{ik}\mathsf{O}_{jk}$ denoting the (skew-symmetric) tensor of angular velocity of the inertial observer with respect to the non-inertial frame. Analogously, $(\text{B.2})_1$ and $(\text{B.5})_1$ immediately imply the transformation rules for the translational and director velocities u_i and w_i^α, respectively, (cf. Sect. 4.4)

$$u_i = \mathsf{O}_{ij}\,(u_j)_{\text{IO}} + \Omega_{ij}\,(x_j - b_j) + \dot{b}_i\ , \qquad w_i^\alpha = \mathsf{O}_{ij}\left(w_j^\alpha\right)_{\text{IO}} + \Omega_{ij}d_j^\alpha\ . \tag{B.7}$$

Scalar, vector and tensor valued fields whose transformation rules have respectively the forms $(\text{B.4})_{1,2,3}$ are called *objective* (also *Euclidean invariant* or (*frame*) *invariant*). In particular, from the point of view of continuum thermodynamics it is natural to suppose that mass density, internal energy, heat flux, chemical production of mass and stresses are objective quantities [266, 275, 317], i.e.,

$$\varrho^\alpha = (\varrho^\alpha)_{\text{IO}}\ , \qquad e^\alpha = (e^\alpha)_{\text{IO}}\ , \qquad q_i^\alpha = \mathsf{O}_{ij}\left(q_j^\alpha\right)_{\text{IO}}\ , \qquad \mathit{\Gamma}^\alpha = (\mathit{\Gamma}^\alpha)_{\text{IO}}\ , \tag{B.8}$$

$$\mathsf{t}_{ij}^\alpha = \mathsf{O}_{ik}\mathsf{O}_{jl}\,(\mathsf{t}_{kl}^\alpha)_{\text{IO}}\ , \qquad \Pi_{ij}^\alpha = \mathsf{O}_{ik}\mathsf{O}_{jl}\,(\Pi_{kl}^\alpha)_{\text{IO}}\ . \tag{B.9}$$

Transformation rules for the specific inertia tensor $\mathsf{I}_{ij}^\alpha = (d^\alpha)^2\,\delta_{ij} - d_i^\alpha d_j^\alpha$ and the specific spin $\sigma_i^\alpha = \epsilon_{ijk}d_j^\alpha\dot{d}_k^\alpha$ can be deduced from $(\text{B.4})_1$ and $(\text{B.5})_1$, viz.

$$\mathsf{I}_{ij}^\alpha = \mathsf{O}_{ik}\mathsf{O}_{jl}\,(\mathsf{I}_{kl}^\alpha)_{\text{IO}}\ , \qquad \sigma_i^\alpha = \mathsf{O}_{ij}\left(\sigma_j^\alpha\right)_{\text{IO}} + \tfrac{1}{2}\mathsf{I}_{ij}^\alpha\epsilon_{jkl}\Omega_{lk}\ , \tag{B.10}$$

where the following identities were utilized in the derivation of $(\text{B.10})_2$:

$$\epsilon_{ipq}\mathsf{O}_{pj}\mathsf{O}_{qk} = \epsilon_{jkl}\mathsf{O}_{il}\ , \qquad \epsilon_{ijk}\epsilon_{ipq} = \delta_{jp}\delta_{kq} - \delta_{jq}\delta_{kp}\ , \qquad \Omega_{kj} = \tfrac{1}{2}\epsilon_{ijk}\epsilon_{ilm}\Omega_{ml}\ . \tag{B.11}$$

Furthermore, from $(4.27)_1$, (4.28), $(\text{B.8})_1$ and (B.10) one readily obtains

$$\mathsf{I}_{ij} = \mathsf{O}_{ik}\mathsf{O}_{jl}\,(\mathsf{I}_{kl})_{\text{IO}}\ , \qquad \sigma_i = \mathsf{O}_{ij}\,(\sigma_j)_{\text{IO}} + \tfrac{1}{2}\mathsf{I}_{ij}\epsilon_{jkl}\Omega_{lk}\,. \tag{B.12}$$

[2] Of course, transformations involving improper orthogonal tensors could also be considered without modification in any of the arguments discussed in this Appendix.

Finally, taking the material time derivative of $(\mathrm{B}.10)_2$ one finds

$$\begin{aligned}\dot{\sigma}_i^\alpha &= \mathsf{O}_{ij}\left(\dot{\sigma}_j^\alpha\right)_{\mathrm{IO}} + \dot{\mathsf{O}}_{ij}\left(\sigma_j^\alpha\right)_{\mathrm{IO}} + \tfrac{1}{2}\dot{\mathsf{I}}_{ij}^\alpha\epsilon_{jpq}\Omega_{qp} + \tfrac{1}{2}\mathsf{I}_{ij}^\alpha\epsilon_{jpq}\dot{\Omega}_{qp}\\ &= \mathsf{O}_{ij}\left(\dot{\sigma}_j^\alpha\right)_{\mathrm{IO}} + \tfrac{1}{2}\left\{\mathsf{I}_{ij}^\alpha\epsilon_{jpq}\dot{\Omega}_{qp} - \Omega_{ik}\mathsf{I}_{kj}^\alpha\epsilon_{jpq}\Omega_{qp} + 2\left(\Omega_{ik}\sigma_k^\alpha + \tfrac{1}{2}\dot{\mathsf{I}}_{ij}^\alpha\epsilon_{jpq}\Omega_{qp}\right)\right\}\,, \quad (\mathrm{B}.13)\end{aligned}$$

and likewise, from the material time derivative of $(\mathrm{B}.12)_2$ there follows

$$\dot{\sigma}_i = \mathsf{O}_{ij}\left(\dot{\sigma}_j\right)_{\mathrm{IO}} + \tfrac{1}{2}\left\{\mathsf{I}_{ij}\epsilon_{jpq}\dot{\Omega}_{qp} - \Omega_{ik}\mathsf{I}_{kj}\epsilon_{jpq}\Omega_{qp} + 2\left(\Omega_{ik}\sigma_k + \tfrac{1}{2}\dot{\mathsf{I}}_{ij}\epsilon_{jpq}\Omega_{qp}\right)\right\}\,. \quad (\mathrm{B}.14)$$

The last three terms of (B.3) and (B.6), as well as the expressions within curly brackets in (B.13) and (B.14), are all different manifestations of the same apparent phenomena, which are respectively called Euler, centrifugal and Coriolis inertial effects, viz.

Table A.1 Inertial effects

	Euler	centrifugal	Coriolis
(B.3)	$\dot{\Omega}_{ij}\left(x_j - b_j\right)$	$-\Omega_{ik}\Omega_{kj}\left(x_j - b_j\right)$	$2\Omega_{ij}\left(v_j - \dot{b}_j\right)$
(B.6)	$\dot{\Omega}_{ij}d_j^\alpha$	$-\Omega_{ik}\Omega_{kj}d_j^\alpha$	$2\Omega_{ij}\dot{d}_j^\alpha$
(B.13)	$\tfrac{1}{2}\mathsf{I}_{ij}^\alpha\epsilon_{jpq}\dot{\Omega}_{qp}$	$-\tfrac{1}{2}\Omega_{ik}\mathsf{I}_{kj}^\alpha\epsilon_{jpq}\Omega_{qp}$	$\left(\Omega_{ik}\sigma_k^\alpha + \tfrac{1}{2}\dot{\mathsf{I}}_{ij}^\alpha\epsilon_{jpq}\Omega_{qp}\right)$

In the table above, it is evident from (B.11) that the last line is just the cross product of the second line by the director d_i^α (cf. also (C.1)).

C Explicit proofs of some outstanding results of Chap. 4

The starting point[3] is the derivation of the missing Coriolis effect appearing in (4.32). Taking the cross product of (4.31) by the director d_j^α and invoking $(\mathrm{B}.4)_1$, (B.11) and (B.13), one obtains

$$\begin{aligned}\epsilon_{ijk}d_j^\alpha l_k^\alpha &= \epsilon_{ijk}d_j^\alpha\left\{\ddot{d}_k^\alpha - \mathsf{O}_{kl}\left(\ddot{d}_l^\alpha\right)_{\mathrm{IO}}\right\}\\ &= \epsilon_{ijk}d_j^\alpha\ddot{d}_k^\alpha - \mathsf{O}_{ij}\left(\epsilon_{jkl}d_k^\alpha\ddot{d}_l^\alpha\right)_{\mathrm{IO}}\\ &= \dot{\sigma}_i^\alpha - \mathsf{O}_{ij}\left(\dot{\sigma}_j^\alpha\right)_{\mathrm{IO}}\\ &= \tfrac{1}{2}\left\{\mathsf{I}_{ij}^\alpha\epsilon_{jpq}\dot{\Omega}_{qp} - \Omega_{ik}\mathsf{I}_{kj}^\alpha\epsilon_{jpq}\Omega_{qp} + 2\left(\Omega_{ik}\sigma_k^\alpha + \tfrac{1}{2}\dot{\mathsf{I}}_{ij}^\alpha\epsilon_{jpq}\Omega_{qp}\right)\right\}\,. \quad (\mathrm{C}.1)\end{aligned}$$

Hence, the multiplication of (C.1) by ϱ^α, with further sum of the product over all α and the aid of $(4.27)_{1,3}$, (4.30) and (4.33), yields

[3] The proofs in this Appendix have been transcribed from [130].

$$\begin{aligned}\sum_{\alpha=1}^{N}\varrho^{\alpha}\epsilon_{ijk}d_j^{\alpha}l_k^{\alpha} &= \sum_{\alpha=1}^{N}\tfrac{1}{2}\Big\{\varrho^{\alpha}\mathsf{I}_{ij}^{\alpha}\epsilon_{jpq}\dot{\Omega}_{qp} - \varrho^{\alpha}\Omega_{ik}\mathsf{I}_{kj}^{\alpha}\epsilon_{jpq}\Omega_{qp} + 2\Big(\varrho^{\alpha}\Omega_{ik}\sigma_k^{\alpha} + \tfrac{1}{2}\varrho^{\alpha}\dot{\mathsf{I}}_{ij}^{\alpha}\epsilon_{jpq}\Omega_{qp}\Big)\Big\} \\ &= \tfrac{1}{2}\left\{\varrho\mathsf{I}_{ij}\epsilon_{jpq}\dot{\Omega}_{qp} - \varrho\Omega_{ik}\mathsf{I}_{kj}\epsilon_{jpq}\Omega_{qp} + 2\left(\varrho\Omega_{ik}\sigma_k + \tfrac{1}{2}\epsilon_{jpq}\Omega_{qp}\sum_{\alpha=1}^{N}\varrho^{\alpha}\dot{\mathsf{I}}_{ij}^{\alpha}\right)\right\} \\ &= \varrho c_i - \tfrac{1}{2}\epsilon_{jpq}\Omega_{qp}\sum_{\alpha=1}^{N}\varrho^{\alpha}\Gamma^{\alpha}\mathsf{I}_{ij}^{\alpha}\,, \end{aligned} \tag{C.2}$$

which proves (4.32). □

The next important result to be derived is (4.34). This involves the definition of the chemical production density of spin, viz. $\epsilon_{ijk}d_j^{\alpha}\psi_k^{\alpha} = \epsilon_{ijk}d_j^{\alpha}(\hat{\psi}_k^{\alpha} + \Gamma^{\alpha}w_k^{\alpha})$ and the assumption that the director interaction force $\hat{\psi}_i^{\alpha}$ is an objective vector (see Sect. 4.4); in other words, $\hat{\psi}_i^{\alpha} = \mathsf{O}_{ij}(\hat{\psi}_j^{\alpha})_{\mathrm{IO}}$. Therefore, using $(4.28)_2$, $(\mathrm{B}.4)_{1,2}$, $(\mathrm{B}.7)_2$, $(\mathrm{B}.8)_4$ and (B.11), it follows that

$$\begin{aligned}\sum_{\alpha=1}^{N}\varrho^{\alpha}\epsilon_{ijk}d_j^{\alpha}\psi_k^{\alpha} &= \sum_{\alpha=1}^{N}\varrho^{\alpha}\epsilon_{ijk}d_j^{\alpha}\left(\hat{\psi}_k^{\alpha} + \Gamma^{\alpha}w_k^{\alpha}\right) \\ &= \sum_{\alpha=1}^{N}\varrho^{\alpha}\left\{\mathsf{O}_{ij}\left[\epsilon_{jpq}d_p^{\alpha}\left(\hat{\psi}_q^{\alpha} + \Gamma^{\alpha}w_q^{\alpha}\right)\right]_{\mathrm{IO}} + \Gamma^{\alpha}\epsilon_{ijk}d_j^{\alpha}\Omega_{kl}d_l^{\alpha}\right\} \\ &= \mathsf{O}_{ij}\sum_{\alpha=1}^{N}\left(\varrho^{\alpha}\epsilon_{jpq}d_p^{\alpha}\psi_q^{\alpha}\right)_{\mathrm{IO}} + \tfrac{1}{2}\epsilon_{jpq}\Omega_{qp}\sum_{\alpha=1}^{\nu}\varrho^{\alpha}\left\{\Gamma^{\alpha}(d^{\alpha})^2\delta_{ij} - \Gamma^{\alpha}d_i^{\alpha}d_j^{\alpha}\right\} \\ &= \mathsf{O}_{ij}\sum_{\alpha=1}^{\nu}\left(\varrho^{\alpha}\epsilon_{jpq}d_p^{\alpha}\psi_q^{\alpha}\right)_{\mathrm{IO}} + \tfrac{1}{2}\epsilon_{jpq}\Omega_{qp}\sum_{\alpha=1}^{\nu}\varrho^{\alpha}\Gamma^{\alpha}\mathsf{I}_{ij}^{\alpha}\,.\square \end{aligned} \tag{C.3}$$

Finally, there remains to prove (4.39) and (4.40). Owing to this, one needs first two auxiliary transformation rules, viz. (cf. $(4.27)_4$, $(\mathrm{B}.4)_2$, $(\mathrm{B}.7)_2$ and (B.11))

$$\begin{aligned}(w^{\alpha})^2 &= \left[\mathsf{O}_{kj}\left(w_j^{\alpha}\right)_{\mathrm{IO}} + \Omega_{kj}d_j^{\alpha}\right]\left[\mathsf{O}_{kp}\left(w_p^{\alpha}\right)_{\mathrm{IO}} + \Omega_{kp}d_p^{\alpha}\right] \\ &= (w^{\alpha})_{\mathrm{IO}}^2 - \Omega_{kj}\Omega_{kp}d_j^{\alpha}d_p^{\alpha} + 2\Omega_{kj}d_j^{\alpha}w_k^{\alpha} \\ &= (w^{\alpha})_{\mathrm{IO}}^2 + \epsilon_{ipq}\Omega_{qp}\epsilon_{ilk}d_l^{\alpha}w_k^{\alpha} - \tfrac{1}{4}\mathsf{I}_{ij}^{\alpha}\epsilon_{ipq}\Omega_{qp}\epsilon_{jlk}\Omega_{kl} \end{aligned} \tag{C.4}$$

and (cf. $(\mathrm{B}.12)_2$)

$$\epsilon_{ipq}d_p^{\alpha}w_q^{\alpha} = \mathsf{O}_{ij}\left(\epsilon_{jpq}d_p^{\alpha}w_q^{\alpha}\right)_{\mathrm{IO}} + \tfrac{1}{2}\mathsf{I}_{ij}^{\alpha}\epsilon_{jpq}\Omega_{qp}\,. \tag{C.5}$$

Of course, both transformations (C.4) and (C.5) remain valid if one substitutes all w_k^{α} by $\dot{d}_k^{\alpha}$, since these two vectors transform in the same way (compare e.g. (C.5) with $(\mathrm{B}.12)_2$). Thence, from $(4.17)_{1,2}$, (4.21), (4.22), $(4.27)_4$, $(\mathrm{B}.4)_2$, $(\mathrm{B}.5)_1$, $(\mathrm{B}.7)_2$, (B.11), (C.3)–(C.5) and the objectivity of the chemical production of internal energy ξ^{α}, one derives

$$
\begin{aligned}
\sum_{\alpha=1}^{N} \varrho^\alpha P^\alpha &= \sum_{\alpha=1}^{\nu} \varrho^\alpha \left\{ \xi^\alpha + \hat{\psi}_k^\alpha \dot{d}_k^\alpha + \tfrac{1}{2} \Gamma^\alpha \left(w^\alpha\right)^2 \right\} \\
&= \sum_{\alpha=1}^{\nu} \varrho^\alpha \Big\{ \left[\xi^\alpha + \hat{\psi}_k^\alpha \dot{d}_k^\alpha + \tfrac{1}{2} \Gamma^\alpha \left(w^\alpha\right)^2 \right]_{\mathrm{IO}} + \hat{\psi}_k^\alpha \Omega_{kl} d_l^\alpha \\
&\qquad + \tfrac{1}{2} \Gamma^\alpha \left(\epsilon_{ipq} \Omega_{qp} \epsilon_{ilk} d_l^\alpha w_k^\alpha - \tfrac{1}{4} \mathsf{I}_{ij}^\alpha \epsilon_{ipq} \Omega_{qp} \epsilon_{jlk} \Omega_{kl} \right) \Big\} \\
&= \sum_{\alpha=1}^{N} \varrho^\alpha \Big\{ \left(P^\alpha\right)_{\mathrm{IO}} + \tfrac{1}{2} \epsilon_{ilk} d_l^\alpha \hat{\psi}_k^\alpha \epsilon_{ipq} \Omega_{qp} \\
&\qquad + \tfrac{1}{2} \Gamma^\alpha \epsilon_{ilk} d_l^\alpha w_k^\alpha \epsilon_{ipq} \Omega_{qp} - \tfrac{1}{8} \Gamma^\alpha \mathsf{I}_{ij}^\alpha \epsilon_{ipq} \Omega_{qp} \epsilon_{jlk} \Omega_{kl} \Big\} \\
&= \sum_{\alpha=1}^{\nu} \varrho^\alpha \left\{ \left(P^\alpha\right)_{\mathrm{IO}} + \tfrac{1}{2} \epsilon_{ilk} d_l^\alpha \psi_k^\alpha \epsilon_{ipq} \Omega_{qp} - \tfrac{1}{8} \Gamma^\alpha \mathsf{I}_{ij}^\alpha \epsilon_{ipq} \Omega_{qp} \epsilon_{jlk} \Omega_{kl} \right\} \\
&= \sum_{\alpha=1}^{\nu} \left\{ \left(\varrho^\alpha P^\alpha\right)_{\mathrm{IO}} + \tfrac{1}{8} \varrho^\alpha \Gamma^\alpha \mathsf{I}_{ij}^\alpha \epsilon_{ipq} \Omega_{qp} \epsilon_{jlk} \Omega_{kl} \right\} . \qquad \text{(C.6)}
\end{aligned}
$$

At last, through the simple switch of all w_k^α in (C.4) and (C.5) by $\dot{d}_k^\alpha$, the expression (4.40) can likewise be proven. □

D Specialized Green–Stokes theorem

Intending to prove Theorem 6.3.1, one starts with the usual expression of the Stokes theorem on an unit spherical surface for an arbitrary (smooth) vector field $\mathsf{a}_i^* = \mathsf{a}_i^*(x_j, t, n_k)$, viz.,

$$
\oint_{\mathcal{S}^2} \epsilon_{ijk} n_i \frac{\partial \mathsf{a}_k^*}{\partial n_j} \, \mathrm{d}^2 n = 0 \, . \qquad \text{(D.7)}
$$

Evidently, a_i^* can be decomposed into orthogonal and parallel parts to n_i as

$$
\mathsf{a}_i^* = \epsilon_{ijk} n_j \mathsf{b}_k^* + \mathsf{c}^* n_i, \qquad \text{(D.8)}
$$

where b_i^* and c^* denote two arbitrary fields. With the aid of (6.32), insertion of (D.8) into (D.7) leads straightforwardly to

$$
\oint_{\mathcal{S}^2} \left(\partial_i \mathsf{b}_i^* - 2 n_i \mathsf{b}_i^* \right) \mathrm{d}^2 n = 0 \, . \qquad \text{(D.9)}
$$

Consequently, for any continuously differentiable field quantity Q_i^* on $\mathcal{S}^2$ such that $\mathsf{Q}_i^* n_i = 0$, (D.9) implies that

$$
\oint_{\mathcal{S}^2} \partial_i \mathsf{Q}_i^* \, \mathrm{d}^2 n = 0 \, , \qquad \text{(D.10)}
$$

which is just the proper form of the completeness assumption (6.31) in the orientation space $\mathcal{S}^2$.

Actually, (D.9) is a particularization of a useful identity which can be easily derived as follows. First, consider the generalization of the Stokes theorem (D.7) for an arbitrary (smooth) tensor field $\mathsf{A}^*_{ijk\ldots lm} = \mathsf{A}^*_{ijk\ldots lm}(x_p, t, n_q)$, viz.,

$$\oint_{\mathcal{S}^2} \epsilon_{ijk} n_i \frac{\partial \mathsf{A}^*_{klm\ldots np}}{\partial n_j} \, \mathrm{d}^2 n = 0 \, . \tag{D.11}$$

A generic decomposition, equivalent to (D.8), is not helpful in this case, due to the complexity of the resulting expression. Therefore, to simplify the calculations, one can restrict attention only to a particular class of tensors, given by

$$\mathsf{A}^*_{klm\ldots np} = \mathsf{B}^*_{lm\ldots n} \epsilon_{krp} n_r \, . \tag{D.12}$$

It must be emphasized that, even though $\mathsf{A}^*_{klm\ldots np}$ is now restricted by (D.12), the lower-order tensor function $\mathsf{B}^*_{lm\ldots n}$ remains *fully arbitrary* (but smooth). Further, inserting (D.12) into (D.11), there follows from (7.5)

$$\oint_{\mathcal{S}^2} \epsilon_{ijk} \epsilon_{krp} n_i \partial_j (\mathsf{B}^*_{lm\ldots n} n_r) \, \mathrm{d}^2 n = 0 \, , \tag{D.13}$$

which can be easily rewritten as

$$\oint_{\mathcal{S}^2} \left(\partial_i \mathsf{B}^*_{jk\ldots l} - 2 n_i \mathsf{B}^*_{jk\ldots l} \right) \mathrm{d}^2 n = 0 \, . \tag{D.14}$$

This identity, presented (without proof) by Condiff & Brenner [78] under the name "specialized Green's theorem on a spherical surface", is essential in many calculations involving integrals of orientational gradients.

E Representation theorems for Chap. 7

All polynomial representations presented below are derived from the representation theorems for isotropic functions found in the literature [275, 380, 381, 421]. They are classified according to the transformation and invariance properties of their respective constitutive functions with respect to inversions of orientation. The tensor field $\mathsf{Q}^*_{ij\ldots pq}$ denotes a generic constitutive quantity and its dependence on x_i and t is omitted here for brevity.

a) $\{e^*, \eta^*, \varepsilon^*\}$ Absolute scalar, $\mathsf{Q}^*(n_i) = \mathsf{Q}^*(-n_i)$:

$$\mathsf{Q}^* = \mathsf{Q}^{*(1)} + \mathsf{Q}^{*(2)} D_{kk} + \mathsf{Q}^{*(3)} n_i D_{ij} n_j \tag{E.1}$$

b) $\{q^*_i, \phi^*_i, \kappa^*_i\}$ Absolute vector, $\mathsf{Q}^*_i(n_j) = \mathsf{Q}^*_i(-n_j)$:

$$\mathsf{Q}^*_i = \mathsf{Q}^{*(1)} \frac{\partial T}{\partial x_i} + \mathsf{Q}^{*(2)} n_i \frac{\partial T}{\partial x_j} n_j \tag{E.2}$$

c) $\{\nu_i^*\}$ Axial vector, $Q_i^*(n_j) = Q_i^*(-n_j)$:

$$Q_i^* = Q^{*(1)}\epsilon_{ijk}H_{jk}^* + Q^{*(2)}\epsilon_{ijk}n_jD_{<kl>}n_l \tag{E.3}$$

d) $\{\xi_i^*, \varphi_i^*\}$ Absolute vector, $Q_i^*n_i = 0$, $Q_i^*(n_j) = -Q_i^*(-n_j)$:

$$Q_i^* = Q^{*(1)}(n_in_j - \delta_{ij})D_{<jk>}n_k + Q^{*(2)}H_{ij}^*n_j \tag{E.4}$$

e) $\left\{\mathsf{t}_{ij}^*\right\}$ Absolute tensor, $\mathsf{Q}_{ij}^*(n_k) = \mathsf{Q}_{ij}^*(-n_k)$:

$$\begin{aligned}\mathsf{Q}_{ij}^* = &\left(\mathsf{Q}^{*(1)} + \mathsf{Q}^{*(2)}D_{kk} + \mathsf{Q}^{*(3)}n_kD_{<kl>}n_l\right)\delta_{ij} + \mathsf{Q}^{*(4)}D_{<ij>} + \\ &+\mathsf{Q}^{*(5)}H_{ij}^* + \left(\mathsf{Q}^{*(6)} + \mathsf{Q}^{*(7)}D_{kk} + \mathsf{Q}^{*(8)}n_kD_{<kl>}n_l\right)n_{<i}n_{j>} + \\ &+\left(\mathsf{Q}^{*(9)} + \mathsf{Q}^{*(10)}\right)n_iD_{<jk>}n_k + \left(\mathsf{Q}^{*(9)} - \mathsf{Q}^{*(10)}\right)n_jD_{<ik>}n_k + \\ &+\left(\mathsf{Q}^{*(11)} + \mathsf{Q}^{*(12)}\right)n_iH_{jk}^*n_k + \left(\mathsf{Q}^{*(11)} - \mathsf{Q}^{*(12)}\right)n_jH_{ik}^*n_k\end{aligned} \tag{E.5}$$

f) $\left\{\mathsf{m}_{ij}^*\right\}$ Axial tensor, $\mathsf{Q}_{ij}^*(n_k) = \mathsf{Q}_{ij}^*(-n_k)$:

$$\mathsf{Q}_{ij}^* = \mathsf{Q}^{*(1)}\epsilon_{ijk}\frac{\partial T}{\partial x_k} + \mathsf{Q}^{*(2)}\epsilon_{ijk}\frac{\partial T}{\partial x_l}n_ln_k + \mathsf{Q}^{*(3)}n_{(i}\epsilon_{j)kl}n_k\frac{\partial T}{\partial x_l} \tag{E.6}$$

g) $\left\{\mathsf{\tau}_{ij}^*\right\}$ Absolute tensor, $\mathsf{Q}_{ij}^*n_j = 0$, $\mathsf{Q}_{ij}^*(n_k) = -\mathsf{Q}_{ij}^*(-n_k)$:

$$\mathsf{Q}_{ij}^* = \mathsf{Q}^{*(1)}\left(n_in_j - \delta_{ij}\right)\frac{\partial T}{\partial x_k}n_k + \mathsf{Q}^{*(2)}\frac{\partial T}{\partial x_k}n_{[i}\delta_{k]j} \tag{E.7}$$

h) $\left\{\mathsf{\varpi}_{ij}^*\right\}$ Axial tensor, $\mathsf{Q}_{ij}^*n_j = 0$, $\mathsf{Q}_{ij}^*(n_k) = -\mathsf{Q}_{ij}^*(-n_k)$:

$$\begin{aligned}\mathsf{Q}_{ij}^* = &\left(\mathsf{Q}^{*(1)} + \mathsf{Q}^{*(2)}D_{kk} + \mathsf{Q}^{*(3)}n_kD_{<kl>}n_l\right)\epsilon_{ijk}n_k + \\ &+\mathsf{Q}^{*(4)}n_i\epsilon_{jkl}H_{kl}^* + \frac{1}{2}\left(\mathsf{Q}^{*(5)} - \mathsf{Q}^{*(6)}\right)\epsilon_{ijk}D_{<kl>}n_l + \\ &+\mathsf{Q}^{*(5)}D_{k<i}\epsilon_{j>kl}n_l + \mathsf{Q}^{*(6)}n_kn_{<i}\epsilon_{j>kl}D_{lp}n_p\end{aligned} \tag{E.8}$$

References

1. Abrahan, R.; J. E. Marsden and T. Ratiu: *Manifolds, Tensor Analysis, and Applications*. 2nd edn. Springer, New York (1988)
2. Acharya, A. and A. J. Beaudoin: Grain-size effect in viscoplastic polycrystals at moderate strains. *J. Mech. Phys. Solids*, **48(10)**, 2213–2230 (2000)
3. Adams, F. D.: *The Birth and Development of the Geological Sciences*. Williams & Wilkins, Baltimore (1938). Unabridged republished by Dover, New York, 1990
4. Aharony, A.; E. L. Hinrichsen; A. Hansen; T. Feder, Jens Jøssang and H. H. Hardy: Effective renormalization group algorithm for transport in oil reservoirs. *Physica A*, **177(1–3)**, 260–266 (1991)
5. Alber, H.-D.: Evolving Microstructure and Homogenization. Tech. Rep. 2051, Technische Universität Darmstadt, Darmstadt (aug 1999). Fachbereich Mathematik
6. Allen, S. J.; C. N. DeSilva and K. A. Klein: Theory of simple deformable directed fluids. *Phys. Fluids*, **10**, 2551–2555 (1967)
7. Allen, S. J. and K. A. Kline: A theory of mixtures with microstructure. *J. Appl. Math. Phys. (ZAMP)*, **20**, 145–155 (1969)
8. Alley, R. B.: Fabrics in polar ice sheets: development and prediction. *Science*, **240**, 493–495 (1988)
9. Alley, R. B.: Flow-law hypothesis for ice-sheet modelling. *J. Glaciol.*, **38**, 245–256 (1992)
10. Arakawa, M. and N. Maeno: Mechanical strength of polycrystalline ice under uniaxial compression. *Cold Reg. Sci. Technol.*, **26**, 215–229 (1997)
11. Aris, R. and G. R. Gavalas: On the theory of reactions in continuous mixtures. *Philos. Trans. Roy. Soc. London A*, **260**, 351–393 (1966)
12. Asaro, R. J.: Micromechanics of crystals and polycrystals. *Adv. Appl. Mech.*, **23**, 1–115 (1983)
13. Asimov, I.: *A Short History of Chemistry*. Greenwood, Westport (1979)
14. Atkin, R. J. and R. E. Craine: Continumm theories of mixtures. Basic theory and historical development. *Quart. J. Mech. Appl. Math.*, **29**, 209–244 (1976)
15. Atkin, R. J. and N. Fox: On the frame-dependence of stress and heat flux in polar fluids. *J. Appl. Math. Phys.*, **24**, 853–860 (1973)
16. Atkins, P. W.: *Physical Chemistry*. Oxford University Press, Oxford (1979)
17. Aveni, A.: *Empires of Time*. I. B. Tauris & Co Ltd, London (1990)
18. Azuma, N.: A flow law for anisotropic ice and its application to ice sheets. *Earth Planet. Sci. Lett.*, **128**, 601–614 (1994)
19. Azuma, N. and K. Goto-Azuma: An anisotropic flow law for ice-sheet ice and its implications. *Ann. Glaciol.*, **23**, 202–208 (1996)
20. Azuma, N. and A. Higashi: Formation processes of ice fabric patterns in ice sheets. *Ann. Glaciol.*, **6**, 130–134 (1985)
21. Badur, J. and H. Stumpf: On the Influence of E. and F. Cosserat on Modern Continuum Mechanics and Field theory. Mitteilungen aus dem Institut für Mechanik 72, Ruhr-Universität Bochum, Bochum (dez 1989)
22. Barlow, W.: Probable nature of the internal symmetry of crystals. *Nature*, **29**, 186–188, 205–207 (1883). P. 404 (1884)
23. Barlow, W.: Über die geometrischen Eigenschaften homogener starrer Strukturen. *Z. Kristallogr. Mineral.*, **23**, 1–63 (1894)
24. Barlow, W.: A mechanical cause of homogeinity of structure and symmetry. *Proc. Roy. Dublin Soc.*, **8**, 527–690 (1897)
25. Barnes, P.; D. Tabor and J. C. F. Walker: The friction and creep of polycrystalline ice. *Proc. Roy. Soc. London A*, **324**, 127–155 (1971)
26. Batchelor, G. K.: *An Introduction to Fluid Dynamics*. Cambridge University Press, Cambridge (1967)
27. Bathurst, R. J. and L. Rothenburg: Micromechanical aspects of isotropic granular assemblies with linear contact interactions. *J. Appl. Mech.*, **55(1)**, 17–23 (1988)
28. Baumgärtner, A. H.: *Theophrastus- Von den Steinen*. Lochner, Nürnberg (1770)
29. Baxter, J.; U. Tüzün; D. Heyes; I. Hayati and P. Fredlund: Stratification in poured granular heaps. *Nature*, **391**, 136 (1998)
30. Bear, J.: *Dynamics of Fluids in Porous Media*. Dover, New York (1988). Originally published by Elsevier, New York, 1972
31. Bear, J. and Y. Bachmat: *Introduction to Modelling of Transport Phenomena in Porous Media*. No. 4 in Theory and Applications of Transport in Porous Media. Kluwer, Dordrecht (1990)

32. Bedford, A. and D. S. Drumheller: Theories of immiscible and structured mixtures. *Int. J. Engng. Sci.*, **21**, 863–960 (1983)
33. Benoit, M.; M. Bernasconi; P. Focher and M. Parrinello: New high-pressure phase of ice. *Phys. Rev. Lett.*, **76**, 2934–2936 (1996)
34. Bentley, W. A. and W. J. Humphreys: *Snow Crystals*. McGraw-Hill, New York (1931)
35. Bergman, T. O.: Variae Crystallorum formae a spatho ortae. *Nova Acta R. Soc. Sci. Ups.*, **1**, 150–155 (1773)
36. Beris, A. N. and B. J. Edwards: *Thermodynamics of Flowing Systems with Internal Structure*. Oxford University Press, Oxford (1994)
37. Bernal, J. D. and R. H. Fowler: A theory of water and ionic solution, with particular reference to hydrogen and hydroxyl ions. *J. Chem. Phys.*, pp. 515–548 (1933)
38. Berne, B. J. and R. Pecora: *Dynamic Light Scattering*. Wiley, New York (1976)
39. Berton, P.: *The Arctic Grail*. Viking, New York (1988)
40. Biot, M. A.: General theory of three-dimensional consolidation. *J. Appl. Phys.*, **12**, 155–164 (1941)
41. Biot, M. A.: Theory of elasticity and consolidation for a porous anisotropic solid. *J. Appl. Phys.*, **26**, 182–185 (1955)
42. Biot, M. A.: Theory of propagation of elastic waves in a fluid-saturated porous solid, I: Low frequency range. *J. Acoust. Soc. Am.*, **28**, 168–178 (1956)
43. Bird, R. B.; O. Hassager; R. C. Armstrong and C. F. Curtiss: *Dynamics of Polymeric Liquids*, vol. II. Wiley, New York (1977)
44. Bird, R. B.; O. Hassager; R. C. Armstrong and C. F. Curtiss: *Dynamics of Polymeric Liquids*, vol. I. Wiley, New York (1977)
45. Blanc, C.: *Grammaire des Arts du Dessin*. Renouard, Paris (1876)
46. Blenk, S.; H. Ehrentraut and W. Muschik: Statistical foundation of macroscopic balances for liquid crystals in alignment tensor formulation. *Physica A*, **174**, 119–138 (1991)
47. Boer, R. d. and W. Ehlers: Theorie der Mehrkomponentenkontinua mit Anwendung auf bodenmechanische Probleme. Forschungsberichte aus der Fachbereich Bauwesen 40, Universität-Gesamthochschule-Essen, Essen (nov 1986)
48. Boltzmann, L.: Zur Theorie der elastischen Nachwirkung. *Ann. Physik*, **7**, 624–654 (1876)
49. Bond, G.; H. Heinrich; W. Broecker; L. Labeyrie; J. McManus; J. Andrews; S. Huon; R. Jantschik; S. Clasen; C. Simet; K. Tedesco; M. Klas; G. Bonani and S. Ivy: Evidence for massive discharges of icebergs into the North Atlantic ocean during the last glacial period. *Nature*, **360**, 245–249 (1992)
50. Bowen, R. M.: Toward a thermodynamics and mechanics. *Arch. Rat. Mech. Anal.*, **24**, 370–403 (1967)
51. Bowen, R. M.: Theory of mixtures. In: *Continuum Physics*, edited by A. C. Eringen, vol. III, pp. 1–127. Academic Press, New York (1976)
52. Bowen, R. M. and D. J. Garcia: On the thermodynamics of mixtures with several temperatures. *Int. J. Engng. Sci.*, **8**, 68–83 (1970)
53. Boyle, R.: *The Sceptical Chymist*. Cadwell, London (1661). Reproduced in T. Birch (Ed.): The Works of the Honourable Robert Boyle, 3rd Edn., Vol. 1, pp. 458-586. Hildesheim: Olms (1965)
54. Boyle, R.: *An essay about the origine & virtues of gems*. Godbid, London (1672). Reproduced in T. Birch (Ed.): The Works of the Honourable Robert Boyle, 3rd Edn., Vol. 3, pp. 512-561. Hildesheim: Olms (1965)
55. Bragg, W. H.: The crystal structure of ice. *Proc. Phys. Soc.*, **34**, 98–103 (1922)
56. Brenner, H.: Rheology of a dilute suspension of axisymmetric Brownian particles. *Int. J. Multiphase Flow*, **1**, 195–341 (1974)
57. Brown Jr., W. F.: *Magnetoelastic Interactions*. Springer, Berlin (1966)
58. Browne, T.: *Pseudoxia Epidemica*. Miller, London (1650)
59. Budd, W. F. and J. T. H.: A review of ice rheology for ice sheet modelling. *Cold Reg. Sci. Technol.*, **16**, 107–144 (1989)
60. Burckhardt, J. J.: *Die Symmetrie der Kristalle*. Birkhäuser, Basel (1988)
61. Bürger, M. J.: Brief history of crystal structure determination. In: *Historical Atlas of Crystallography*, edited by J. Lima-de Faria, pp. 109–124. Kluwer, Dordrecht (1990)
62. Burgers, J. M.: On the motion of small particles of elongated form suspended in a viscous liquid. *Kon. Ned. Akad. Wet., Verhand. (Eerte Sectie)*, **16(4)**, 113–184 (1938). In: Second report on viscosity and plasticity, Ch. III
63. Burke, J. G.: *Origins of the Science of Crystals*. University of California Press, Berkeley (1966)
64. Campbell, C. S.: Boundary interactions for two-dimensional granular flows. Part 1. Flat Boundaries, asymmetric stresses and couple stresses. *J. Fluid Mech.*, **247**, 111–136 (1993)
65. Campbell, C. S.: Boundary interactions for two-dimensional granular flows. Part 1. Roughened Boundaries. *J. Fluid Mech.*, **247**, 137–156 (1993)
66. Campbell, C. S. and A. Gong: The stress tensor in a two-dimensional granular shear flow. *J. Fluid Mech.*, **164**, 107–125 (1986)
67. Cardano, G.: *De Subtilitate*. Petreius, Nürnberg (1550)
68. Castelnau, O.; G. R. Canova and P. Lebensohn, R. A. Duval: Modelling viscoplastic behavior of anisotropic polycrystalline ice with a self-consistent approach. *Acta Mater*, **45**, 4823–4834 (1997)

69. Castelnau, O. and P. Duval: Simulations of anisotropy and fabric development in polar ice. *Ann. Glaciol.*, **20**, 277–282 (1995)
70. Castelnau, O.; P. Duval; R. A. Lebensohn and G. R. Canova: Viscoplastic modelling of texture development in polycrystalline ice with a self-consistent approach: comparison with bound estimates. *J. Geophys. Res.*, **101**, 13851–13868 (1996)
71. Castelnau, O.; H. Shoji; H. Milsch; A. Mangeney; P. Duval; A. Miyamoto; K. Kawada and O. Watanabe: Anisotropic behavior of GRIP ices and flow in Central Greenland. *Earth Planet. Sci. Lett.*, **154**, 307–322 (1998)
72. Castelnau, O.; T. Thorsteinsson; J. Kipfstuhl; P. Duval and G. R. Canova: Modelling fabric development along the GRIP ice core, central Greenland. *Ann. Glaciol.*, **23**, 194–201 (1996)
73. Chadwick, P.: *Continuum Mechanics*. Dover, Mineola, New York (1999)
74. Chevreul, M.-E.: *De la Loi du Contraste Simultané des Couleurs, et de l'Assortiment des Objets Colorés*. Pitois-Levrault, Paris (1839)
75. Chorlton, W.: *Planet Earth Ice Ages*. Time-Life Books, Alexandria (1983)
76. Christoffersen, J.; M. M. Mehrabadi and S. Nemat-Nassar: A micromechanical description of granular material behavior. *J. Appl. Mech.*, **48(2)**, 339–344 (1981)
77. Clarke, G. K. C. and D. I. La Prairie: Modelling iceberg drift and ice-rafted sedimentation. In: *Continuous Mechanics and Applications in Geophysics and the Environment*, edited by B. Straughan; R. Grve; H. Ehrentraut and Y. Wang, pp. 183–200. Springer, Heidelberg (2001)
78. Condiff, D. W. and H. Brenner: Transport mechanics in systems of orientable particles. *Phys. Fluids*, **12**, 539–551 (1969)
79. Cosserat, E. M. P. and F. Cosserat: *Théorie des Corps Déformables*. Hermann, Paris (1909)
80. Cowin, S. C.: The characteristic lenght of a polar fluid. In: *Mechanics of Generalized Continua*, edited by E. Kroner. Springer, Berlin (1968)
81. Cowin, S. C.: Polar fluids. *Phys. Fluids*, **11**, 1919–1927 (1968)
82. Cowin, S. C.: The theory of polar fluids. *Adv. Appl. Mech.*, **14**, 279–347 (1974)
83. Cuffey, K. M.; H. Conway; A. Gades; B. Hallet; C. F. Raymond and S. Whitlow: Deformation properties of subfreezing glacier ice: role of crystal size, chemical impurities and rock particles inferred from in situ measurements. *J. Geophys. Res.*, **105(B12)**, 27895–27915 (2000)
84. Curtiss, C. F.: Kinetic theory of nonspherical molecules. *J. Chem. Phys.*, **24**, 225–241 (1956)
85. Dahler, J. S.: Transport phenomena in a fluid composed of diatomic molecules. *J. Chem. Phys.*, **30**, 1447–1475 (1959)
86. Dahler, J. S.; S. Fesciyan and N. Xystris: Rheological properties of a semidilute solution of rodlike macromolecules II: transient flows. *Macromolecules*, **16**, 1673–1677 (1983)
87. Dahler, J. S. and L. E. Scriven: Angular momentum of continua. *Nature*, **192**, 36–37 (oct 1961)
88. Dahler, J. S. and L. E. Scriven: Theory of structured continua I. General consideration of angular momentum and polarization. *Proc. Roy. Soc. London A*, **275**, 504–527 (1963)
89. Dalton, J.: *A New System of Chemical Philosophy*, vol. 1. Russell, Manchester (1808)
90. Darcy, H.: *Les Fontaines Publiques de la Ville de Dijon*. Dalmont, Paris (1856)
91. de Boer, R.: Highlights in the historical development of the porous media theory. *Appl. Mech. Rev.*, **49**, 201–262 (1996)
92. de Gennes, P. G. and J. Prost: *The Physics of Liquid Crystals*. 2nd edn. Clarendon Press, Oxford (1993)
93. De Groot, S. R. and P. Mazur: *Non-Equilibrium Thermodynamics*. North-Holland, Amsterdam (1962)
94. De la Chapelle, S.; O. Castelnau; V. Lipenkov and P. Duval: Dynamic recrystallization and texture development in ice as revealed by the study of deep ice cores in Antarctica and Greenland. *J. Geophys. Res.*, **103**, 5091–5105 (1998)
95. Debye, P.: *Polare Molekeln*. Hirzel, Leipzig (1929)
96. Denbigh, K. G.: *The Principles of Chemical Equilibrium*. Cambridge University Press, Cambridge (1955)
97. Dennison, D. M.: The crystal structure of ice. *Phys. Rev.*, **17**, 20–22 (1921)
98. Diebels, S.: A micropolar theory of porous media: consitutive modelling. *Transport in Porous Media*, **34**, 193–208 (1999)
99. Dillamore, I. L.; C. J. E. Smith and W. B. Hutchinson: Transition bands and recrystallization in metals. *Proc. Roy. Soc. London A*, **329**, 405–420 (1972)
100. Doi, M.: Rotational Relaxation time of rigid rod-like macromolecule in concentrated solution. *J. Physique*, **36**, 607–611 (1975)
101. Doi, M.: Molecular dynamics and rheological properties of concentrated solutions of rodlike polymers in isotropic and liquid crystalline phases. *J. Polymer Sci.*, **19**, 229–243 (1981)
102. Doi, M. and S. F. Edwards: Dynamics of rod-like macromolecules in concentrated solution. *J. Chem. Soc., Faraday Trans. II*, **74**, 560–570, 918–932 (1978)
103. Doi, M. and S. F. Edwards: *The Theory of Polymer Dynamics*. Clarendon Press, Oxford (1986)
104. Donder, T. E. d.: *L'Affinité*. Gauthier-Villars, Paris (1927)
105. Drescher, A. and G. De Josselin De Jong: Photoelastic verification of a mechanical model for the flow of a granular material. *J. Mech. Phys. Solids*, **20**, 337–351 (1972)
106. Drew, D. A. and S. L. Passman: *Theory of Multicomponent Fluids*. Springer, New York (1999)

107. Dreyer, W.: Maximisation of the entropy in non-equilibrium. *J. Phys. A. Math. Gen.*, **20**, 6505–6517 (1987)
108. Duhem, P.: Le potentiel thermodynamique et la pression hydrostatique. *Ann. Sci. École Norm. Sup.*, **10**, 187–230 (1893)
109. Dunwoody, N. T.: Balance laws for liquid crystal mixtures. *Journal Appl. Math. Phys. (ZAMP)*, **26**, 105–111 (1975)
110. Dunwoody, N. T. and I. Müller: A thermodynamic theory of two chemically reacting ideal gases with different temperatures. *Arch. Rat. Mech. Anal.*, **29**, 344–369 (1968)
111. Duran, J.: *Sands, Powders, and Grains*. Springer, New York (2000)
112. Duval, P.; L. Arnaud and O. Brissaud: Deformation and recrystallization processes of ice from polar ice sheets. *Ann. Glaciol.*, **30**, 83–87 (2000)
113. Duval, P.; M. F. Ashby and I. Anderman: Rate-controlling processes in the creep of polycrystalline ice. *J. Phys. Chem.*, **87**, 4066–4074 (1983)
114. Duval, P. and O. Castelnau: Dynamic recrystallization of ice in polar ice sheets. *J. Phys. IV (Paris), colloq. C3*, **5**, 197–205 (1995)
115. Eckart, C.: The thermodynamics of irreversible processes II. Fluid mixtures. *Phys. Rev.*, **58**, 269–275, 924 (1940)
116. Ehlers, W.: *Poröse Medien*. Habilitationsschrift, Universität-Gesamthochschule-Essen, Essen (1989)
117. Ehlers, W.; S. Diebels and T. Michelitsch: Microscopic modelling of granular materials taking into account particle rotations. In: *Continuous and Discontinuous Modelling of Cohesive-Frictional Materials*, edited by P. A. Vermeer; S. Diebels; W. Ehlers; H. J. Herrmann; S. Luding and E. Ramm, pp. 259–274. Springer, Berlin (2001)
118. Ehrentraut, H.: Anisotropic fluids: from liquid crystals to granular materials. In: *Continuous Mechanics and Applications in Geophysics and the Environment*, edited by B. Straughan; R. Greve; H. Ehrentraut and Y. Wang, pp. 18–43. Springer, Heidelberg (2001)
119. Einstein, A.: Letter to Marcel Grossmann, 14 April 1901. In: *The Collected Papers of Albert Einstein*, edited by J. Stachel, vol. I, pp. 290–291. Princeton University Press, Princeton (1987)
120. Ericksen, J. L.: Anisotropic fluids. *Arch. Rational Mech. Anal.*, **4**, 231–237 (1960)
121. Ericksen, J. L.: Conservation laws for liquid crystals. *Trans. Soc. Rheol.*, **5**, 23–34 (1961)
122. Ericksen, J. L.: Instability in Couette flow of anisotropic fluids. *Q. J. Mech. Appl. Math.*, **19** (1966)
123. Eringen, A. C.: *Microcontinuum Field Theories*. Springer, New York (1999)
124. Eringen, A. C. and J. D. Ingram: A continuum theory of chemically reacting media I. *Int. J. Engng. Sci.*, **3**, 197–212 (1965)
125. Eringen, A. C. and C. B. Kafadar: Polar field theories. In: *Continuum Physics*, edited by A. C. Eringen, vol. IV, pp. 1–73. Academic Press, New York (1976)
126. Eringen, A. C. and G. A. Maugin: *Electrodynamics of Continua*, vol. 1. Springer, New York (1990)
127. Eringen, A. C. and G. A. Maugin: *Electrodynamics of Continua*, vol. 2. Springer, New York (1990)
128. Evans, R. C.: *Einführung in die Kristallchemie*. de Gruyter, Berlin (1976). Translated by J. Pickardt and E. Riedel
129. Faria, S. H.: Mixtures with continuous diversity: general theory and application to polymer solutions. *Continuum Mech. Thermodyn.*, **13**, 91–120 (2001)
130. Faria, S. H.: Solution of Müller's paradox of frame dependence in mixtures of polymeric liquid crystals. *Continuum Mech. Thermodyn.* (in press)
131. Faria, S. H. and K. Hutter: The challenge of polycrystalline ice dynamics. In: *Advances in Thermal Engineering and Sciences for Cold Regions*, edited by S. Kim and D. Jung, pp. 3–31. Society of Air-Conditioning and Refrigerating Engineers of Korea (SAREK), Seoul (2001)
132. Faria, S. H. and K. Hutter: A systematic approach to the thermodynamics of single and mixed flowing media with microstructure. Part I: balance equations and jump conditions. *Continuum Mech. Thermodyn.*, **14**, 459–481 (2002)
133. Faria, S. H. and G. M. Kremer: Some aspects in the thermodynamic theory of polar fluids. *ARI*, **50**, 105–109 (1997). Corrigendum ibid. (1998) vol.51, p.103
134. Faria, S. H. and G. M. Kremer: A constitutive theory for ferrofluids. *Continuum Mech. Thermodyn.*, **11**, 297–306 (1999)
135. Faria, S. H.; G. M. Kremer and K. Hutter: On the inclusion of recrystallization processes in the modeling of induced anisotropy in ice sheets: a thermodynamicist's point of view. *Ann. Glaciol.*, **37** (in press)
136. Ferry, J. D.: *Viscoelastic Properties of Polymers*. 2nd edn. Wiley, New York (1970)
137. Fesciyan, S. and J. S. Dahler: Screened hydrodynamic interactions in a semidilute solution of rodlike macromolecules. *Macromolecules*, **15**, 517–520 (1982)
138. Fick, A.: Über Diffusion. *Ann. Physik*, **94**, 59–86 (1855)
139. Fillunger, P.: Auftrieb und Unterdruck in Tallsperren. *Die Wasserwirtschaft*, **22**, 334–336, 371–377, 388–390 (1929)
140. Fillunger, P.: Zur Frage des Auftriebs in Tallsperren. *Die Wasserwirtschaft*, **23**, 63–66 (1930)
141. Fletcher, N. H.: *The Chemical Physics of Ice*. Cambridge University Press, Cambridge (1970)
142. Fokker, P. A.: General anisotropic effective medium theory for the effective permeability of heterogeneous reservoirs. *Transport in Porous Media*, **44**, 205–218 (2001)

143. Fowler, A.: Modelling the flow of glaciers and ice sheets. In: *Continuum Mechanics and Applications in Geophysics and the Environment*, edited by B. Straughan; R. Greve; H. Ehrentraut and Y. Wang, pp. 201–221. Springer, Heidelberg (2001)
144. Fowler, R. Guggenheim, E. A.: *Statistical Thermodynamics*. Cambridge University Press, Cambridge (1965)
145. Frank, F. C.: On the theory of liquid crystals. *Discuss. Faraday Soc.*, **25**, 19–28 (1958)
146. Frank, F. C.: Descartes' observations on the Amsterdam snowfalls of 4, 5, 6 and 9 February 1635. *J. Glaciology*, **13**, 535–539 (1974)
147. Frank, F. C.: Snow crystals. *Contemp. Phys.*, **23**, 3–22 (1982)
148. Frank, F. C. and W. T. Read: Multiplication processes for slow moving dislocations. *Phys. Rev.*, **79**, 722–723 (1950)
149. Fried, E. and S. Sellers: The Debye theory of rotary diffusion: history, derivation, and generalizations. *Arch. Rational Mech. Anal.*, **158**, 1–27 (2001)
150. Frost, H. J. and M. F. Ashby: *Deformation-mechanism Maps*. Pergamon, Oxford (1982)
151. Frujita, S.; M. Nakawo and S. Mae: Orientation of the 700m Mizuho core and its strain story. *Proc. NIPR Symp. Polar Meteo. Glaciol.*, **1**, 122–131 (1987)
152. Fukuda, A.; T. Hondoh and A. Higashi: Dislocation mechanisms of plastic deformation of ice. *J. Phys. (Paris)*, **48**, 163–173 (1987)
153. Fung, Y. C.: *Foundations of Solid Mechanics*. Prentice-Hall, Englewood Cliffs (1965)
154. Gagliardini, O. and J. Meyssonnier: Plane flow of an ice sheet exhibiting strain-induced anisotropy. In: *Advances in Cold-Region Thermal Engineering and Sciences*, edited by K. Hutter; Y. Wang and H. Beer, pp. 171–182. Springer, Berlin (1999)
155. Gagliardini, O. and J. Meyssonnier: Simulation of anisotropic ice flow and fabric evolution along the GRIP-GISP2 flow line, central Greenland. *Ann. Glaciol.*, **30**, 217–223 (2000)
156. Gaio, D. C. and G. M. Kremer: Kinetic theory for polyatomic dense gases of rough spherical molecules. *J. Non-Eq. Thermodyn.*, **16**, 357–379 (1991)
157. Garner, F. H. and A. H. Nissan: Rheological properties of high-viscosity solutions of long molecules. *Nature*, **158**, 634–635 (1946)
158. Giesekus, H.: *Phänomenologische Rheologie*. Springer, Heidelberg (1994)
159. Gilbert, W.: *De Magnete*. Short, London (1600)
160. Glen, J. W.: The creep of polycrystalline ice. *Proc. Roy. Soc. London A*, **228**, 519–538 (1953)
161. Glen, J. W.: The flow law of ice: A discussion of the assumptions made in glacier theory, their experimental foundations and consequences. *IASH*, **47**, 171–183 (1958)
162. Glen, J. W.: The effect of hydrogen disorder on dislocation movement and plastic deformation of ice. *Phys. Kondens. Mater*, **7**, 43–51 (1968)
163. Glen, J. W.: The mechanics of ice. Cold regions science and engineering monograph II C2b, U. S. Army CRREL, Hanover (1975)
164. Glen, J. W. and M. F. Perutz: The growth and deformation of ice crystals. *J. Glaciol.*, **2**, 397–403 (1954)
165. Gödert, G.: A meso-macro model for the description of induced anisotropy of natural ice, including grain interaction. In: *Advances in Cold-Region Thermal Engineering and Sciences*, edited by K. Hutter; Y. Wang and H. Beer, pp. 183–196. Springer, Berlin (1999)
166. Gödert, G. and K. Hutter: Induced anisotropy in large ice sheets: theory and its homogenization. *Continuum Mech. Thermodyn.*, **13**, 91–120 (1998)
167. Gödert, G. and K. Hutter: Material update procedure for planar transient flow of ice with evolving anisotropy. *Ann. Glaciol.*, **30**, 107–114 (2000)
168. Goldsby, D. L. and D. L. Kohlstedt: Grain boundary sliding in fine-grained ice. *Scripta Mater*, **37**, 1399–1406 (1997)
169. Goodman, D. J.; H. J. Frost and M. F. Ashby: The plasticity of polycrystalline ice. *Philos. Mag.*, **43**, 665–695 (1981)
170. Gow, A. J.; D. A. Meese; R. B. Alley; J. J. Fitzpatrick; S. Anandakrishnan; G. A. Woods and B. C. Elder: Physical and structural properties of the Greenland ice sheet project 2 ice core: a review. *J. Geophys. Res.*, **102**, 26559–26575 (1997)
171. Grad, H.: Statistical mechanics, thermodynamics and fluid dynamics of systems. *Commun. Pure Appl. Math.*, **5**, 455–494 (1952)
172. Gray, J. M. N. T. and K. Hutter: Pattern formation in granular avalanches. *Continuum Mech. Thermodyn.*, **9**, 341–345 (1997)
173. Gray, J. M. N. T. and Y. C. Tai: Particle size segregation, granular shocks and stratification patterns. In: *Physics of Dry Granular Media*, edited by H. J. Herrmann; J.-P. Hovi and S. Luding, NATO science series: E, pp. 697–702. Kluwer, Dordrecht (1998)
174. Gray, W. G.: Elements of a systematic procedure for the derivation of macroscale conservation equations for multiphase flow in porous media. In: *Kinetic and Continuum Theories of Granular and Porous Media*, edited by K. Hutter and K. Wilmański, no. 400 in CISM courses and lectures series, pp. 67–129. Springer, Wien (1999)
175. Gray, W. G. and S. M. Hassanizadeh: Paradoxes and realities in unsaturated flow theory. *Water Resour. Res.*, **27**, 1847–1854 (1991)

176. Gray, W. G. and S. M. Hassanizadeh: Unsaturated flow theory including interfacial phenomena. *Water Resour. Res.*, **27(8)**, 1855–1863 (1991)
177. Green, A. E. and N. Laws: Global properties of mixtures. *Arch. Rat. Mech. Anal.*, **43**, 45–61 (1971)
178. Green, A. E. and P. M. Naghdi: A dynamical theory of interacting continua. *Int. J. Engng. Sci.*, **3**, 231–241 (1965)
179. Green, A. E.; P. M. Naghdi and R. S. Rivlin: Directors and multipolar displacements in continuum mechanics. *Int. J. Engng. Sci.*, **2**, 611–620 (1965)
180. Green, A. E. and R. S. Rivlin: The mechanics of non-linear materials with memory, Part I. *Arch. Rat. Mech. Anal.*, **1**, 1–21 (1957)
181. Green, A. E. and R. S. Rivlin: The mechanics of non-linear materials with memory, Part III. *Arch. Rat. Mech. Anal.*, **4**, 387–404 (1960)
182. Green, A. E.; R. S. Rivlin and A. J. M. Spencer: The mechanics of non-linear materials with memory, Part II. *Arch. Rat. Mech. Anal.*, **3**, 82–90 (1959)
183. Green, M. S. and A. V. Tobolsky: A new approach to the theory of relaxing polymeric media. *J. Chem. Phys.*, **14**, 80–82 (1946)
184. Greene, J. C. and J. G. Burke: The science of minerals in the age of Jefferson. *Trans. Amer. Philos. Soc.*, **68**, 1–113 (1978)
185. Greensmith, H. W. and R. S. Rivlin: Measurements of the normal-stress effect in solutions of polyisobutylene. *Nature*, **168**, 664–667 (1951)
186. Greensmith, H. W. and R. S. Rivlin: The hydrodynamics of non-Newtonian fluids, III. The normal-stress effect in high-polymer solutions. *Phil. Trans. Royal Soc. London A*, **245**, 399–429 (1953)
187. Gregorietti, G.: Jewelry. In: *The New Encyclopaedia Britannica*, edited by P. W. Goetz, 15th edn. Encyclopaedia Britannica, Chicago (1993)
188. Groma, I.: Link between the microscopic and mesoscopic length-scale description of the collective behavior of dislocations. *Phys. Rev.*, **B56(10)**, 5807–5813 (1997)
189. Gurtin, M. E.: On the thermodynamics of chemically reacting fluid mixtures. *Arch. Rat. Mech. Anal.*, **43**, 198–212 (1971)
190. Haas, M. P. d.; M. Kunst; J. M. Warman and J. B. Verberne: Nanosecond time-resolved conductivity studies of pulse-ionized ice.1.The mobility and trapping of conduction-band electrons in H_2O and D_2O ice. *J. Chem. Phys.*, **87**, 4089–4092 (1983)
191. Haase, R.: Thermodynamische Eigenshaften binärer und ternärer Flüssigkeitsgemische. *Z. Elektrochem.*, **55(1)**, 29–38 (1951)
192. Habib, P.: *An Outline of Soil and Rock Mechanics*. Cambridge University Press, Cambridge (1983)
193. Hadamard, J.: Sur les opérations fonctionnelles. *C. R. Acad. Sci. (Paris)*, **136**, 351–354 (1903)
194. Hadamard, J.: *Leçons sur le Calcul des Variations*. Hermann, Paris (1910)
195. Hallett, J. and B. J. Mason: The influence of temperature and supersaturation on the habit of ice crystals grow from the vapour. *Proc. Roy. Soc. London A*, **247**, 440–453 (1958)
196. Hamilton, W. R.: *Lectures on Quaternions*. Hodges and Smith, Dublin (1853)
197. Hand, G. L.: A theory of anisotropic fluids. *J. Fluid Mech.*, **13**, 33–47 (1962)
198. Hansen, N.: Deformation microstructures. *Scr. Metall. Mater.*, **27**, 1447–1452 (1992)
199. Harren, S. V. and R. J. Asaro: Nonuniform deformations in polycrystals and aspects of the validity of the Taylor model. *J. Mech. Phys. Solids*, **37**, 191–232 (1989)
200. Hassanizadeh, S. M. and W. G. Gray: Mechanics and thermodynamics of multiphase flow in porous media including interphase boundaries. *Adv. Water Resources*, **13(4)**, 169–186 (1990)
201. Haüy, R.-J.: *Essai d'une théorie sur la structure des cristaux*. de la Rochelle, Paris (1784)
202. Haüy, R.-J.: *Traité de Minéralogie*, vol. 1-5. Louis, Paris (1801)
203. Haüy, R.-J.: *Traité de Cristallographie*, vol. 1-3. Bachelier & Huzard, Paris (1822)
204. Heinrich, H.: Origin and consequences of cyclic ice rafting in the Northeast Atlantic ocean during the past 130,000 years. *Quat. Res.*, **29**, 142–152 (1988)
205. Helmholtz, H. v.: *Handbuch der Physiologischen Optik*. Voss, Leipzig (1867)
206. Herrmann, H. J. and S. Luding: Modelling granular media on the computer. *Continuum Mech. Thermodyn.*, **10(4)**, 189–231 (1998)
207. Hinch, E. J. and L. G. Leal: The effect of Brownian motion on the rheological properties of a suspension of non-spherical particles. *J. Fluid Mech.*, **52**, 683–712 (1972)
208. Hinch, E. J. and L. G. Leal: Time-dependent shear flows of a suspension of particles with weak Brownian rotations. *J. Fluid Mech.*, **57**, 753–767 (1973)
209. Hirschfelder, J. O.; C. F. Curtiss and R. B. Bird: *Molecular Theory of Gases and Liquids*. Wiley, New York (1954)
210. Hobbs, P. V.: *Ice Physics*. Clarendon, Oxford (1974)
211. Høeg, P.: *Miss Smilla's Feeling for Snow*. Flamingo, London (1994)
212. Hoffman, O. and G. Sachs: *Introduction to the Theory of Plasticity for Engineers*. McGraw-Hill, New York (1953)
213. Holzapfel, W. B.: Evasive ice X and heavy fermion ice XII: facts and fiction about high-pressure ices. *Physica B*, **265**, 113–120 (1999)
214. Hondoh, T.; H. Iwamatsu and S. Mae: Dislocation mobility for nonbasal glide in ice measured by in situ X-ray topography. *Phylos. Mag.*, **62**, 89–102 (1990)

215. Hooke, R.: *Micrographia*. Martyn & Allestry, London (1665)
216. Humphreys, F. J. and M. Hatherly: *Recrystallization and Related Annealing Phenomena*. Pergamon, Oxford (1996)
217. Hutter, K.: A thermodynamic theory of fluids and solids in electromagnetic fields. *Arch. Rat. Mech. Anal.*, **64**, 269–298 (1977)
218. Hutter, K.: The effect of longitudinal strain on the shear stress of an ice sheet. *J. Glaciol.*, **25**, 39–56 (1981)
219. Hutter, K.: Dynamics of glaciers and large ice masses. *Ann. Rev. Fluid Mech.*, **14**, 87–130 (1982)
220. Hutter, K.: *Theoretical Glaciology*. Reidel, Dordrecht (1983)
221. Hutter, K.: The physics of ice-water phase change surfaces. In: *Modelling Macroscopic Phenomena at Liquid Boundaries*, edited by W. Kosinski and A. I. Murdoch, CISM courses and lectures series, pp. 159–216. Springer, Wien (1991)
222. Hutter, K.: Order and disorder in granular materials. In: *Kinetic and Continuum Theories of Granular and Porous Media*, edited by K. Hutter and K. Wilmański, no. 400 in CISM courses and lectures series, pp. 1–65. Springer, Wien (1999)
223. Hutter, K. and I. Müller: On mixtures of relativistic fluids. *Helv. Phys. Acta*, **48**, 675–698 (1975)
224. Hutter, K. and K. R. Rajagopal: On flows of granular materials. *Continuum Mech. Thermodyn.*, **6**, 81–139 (1994)
225. Hutter, K. and A. A. F. v. d. Ven: *Field Matter Interactions in Thermoelastic Solids*. Springer, Berlin (1978)
226. Iverson, R. M.: The physics of debris flows. *Reviews of Geophysics*, **35(3)**, 245–296 (1997)
227. Iverson, R. M.; M. E. Reid; N. R. Iverson; R. G. LaHusen; M. Logan; J. E. Mann and D. L. Brien: Acute sensitivity of landslide rates to initial soil porosity. *Science*, **290(5491)**, 513–516 (2000)
228. Jacka, T. H.: Laboratory studies on relationships between ice crystal size and flow rate. *Cold Reg. Sci. Technol.*, **10**, 31–42 (1984)
229. Jacka, T. H. and L. Jun: Flow rates and crystal orientation fabrics in compression of polycrystalline ice at low temperatures and stresses. In: *Physics of Ice Core Records*, edited by T. Hondoh, pp. 83–102. Hokkaido University Press, Sapporo (2000)
230. Jaumann, G.: Geschlossenes System physikalischer und chemischer Differentialgesetze. *Sitzungsber. Akad. Wiss. (Wien), Math.- Naturwiss. Kl., Abt. IIa*, **120**, 385–530 (1911)
231. Jeffery, G. B.: The motion of ellipsoidal particles immersed in a viscous fluid. *Proc. Roy. Soc. London A*, **102**, 161–179 (1922)
232. Jenkins, J. T.: Flows of nematic liquid crystals. *Ann. Rev. Fluid Mech.*, **10**, 197–219 (1978)
233. Jenkins, J. T. and L. La Ragione: Paricle spin in anisotropic granular materials. *Int. J. Solids Struct.*, **38**, 1063–1069 (2001)
234. Jenkins, J. T. and S. B. Savage: A theory for the rapid flow of identical, smooth, nearly elastic particles. *J. Fluid Mech.*, **130**, 187–202 (1983)
235. Jones, S. J. and J. W. Glen: The mechanical properties of single crystals of pure ice. *J. Glaciol.*, **8**, 463–473 (1969)
236. Jun, L.; T. H. Jacka and W. F. Budd: Deformation rates in combined compression and shear for ice which is initially isotropic and after the development of strong anisotropy. *Ann. Glaciol.*, **23**, 247–252 (1996)
237. Jun, L.; T. H. Jacka and W. F. Budd: Strong single-maximum crystal fabrics developed in ice undergoing shear with unconstrained normal deformation. *Ann. Glaciol.*, **30**, 88–92 (2000)
238. Kamb, B.: Experimental recrystallization of ice under stress. In: *Flow and Fracture of Rocks*, edited by H. C. Heard; I. Y. Borg; N. L. Carter and C. B. Raleigh, no. 16 in Geophysical Monograph, pp. 211–241. American Geophysical Union, Washington, DC (1972)
239. Kamb, W. B.: The glide direction in ice. *J. Glaciol.*, **3**, 1097–1106 (1961)
240. Kelly, P. D.: A reacting continuum. *Int. J. Engng. Sci.*, **2**, 129–153 (1964)
241. Kepler, J.: *Strena seu de nive sexangula*. Tampach, Frankfurt (1611)
242. Kirchner, N. P.: Thermodynamically consistent modelling of abrasive granular materials. I Non-equilibrium theory. *Proc. R. Soc. London A*, **458**, 2153–2176 (2002)
243. Kirchner, N. P. and K. Hutter: Thermodynamic modelling of granular continua exhibiting quasi-static frictional behavior with abrasion. In: *Mathematical Models of Granular and Porous Materials*, edited by G. Capriz; G. Ghionna and G. Giovine, Modelling and Simulation in Science, Engineering and Technology series. Birkhäuser, Basel (2001)
244. Kirchner, N. P. and K. Hutter: Elasto-plastic behaviour of a granular material with an additional scalar degree of freedom. In: *Porous Media: Theory, Experiments and Numerical Applications*, edited by W. Ehlers and J. Bluhm, Modelling and Simulation in Science, Engineering and Technology series, pp. 147–168. Springer, Heidelberg (2002)
245. Kirkwood, J. G. and P. L. Auer: The visco-elastic properties of solutions of rod-like macromolecules. *J. Chem. Phys.*, **19**, 281–283 (1951)
246. Kirkwood, J. G. and R. J. Plock: Non-Newtonian viscoelastic properties of rod-like macromolecules in solution. *J. Chem. Phys.*, **24**, 665–669 (1956)
247. Kocks, U. F.; C. N. Tomé and H.-R. Wenk: *Texture and Anisotropy*. Cambridge University Press, Cambridge (1998)

248. Kotaka, T.: Note on the normal stress effect in the solution of rodlike molecules. *J. Chem. Phys.*, **30**, 1566–1567 (1959)
249. Koza, M.; H. Schober; A. Tölle; F. Fujara and T. Hansen: Formation of ice XII at different conditions. *Nature*, **397**, 660–661 (1999)
250. Kröner, E.: Initial studies of a plasticity theory based upon statistical mechanics. In: *Inelastic Behavior of Solids*, edited by M. F. Kanninen; W. F. Adler; A. R. Rosenfield and R. I. Jafee, pp. 137–148. McGraw-Hill, New York (1970)
251. Kröner, E.: Benefits and shortcomings of the continuous theory of dislocations. *Int. J. Solids Struct.*, **38(6–7)**, 1115–1134 (2001)
252. Ktitarev, D.; G. Gödert and K. Hutter: Cellular automaton model for recrystallization, fabric and texture development in polar ice. *J. Geophys. Res.*, **107(B8)**, doi:10.1029/2001JB000621 (2003)
253. Kuhn, W. and H. Kuhn: Die Abhängigkeit der Viskosität vom Strömungsgefälle bei hochverdünnten Suspensionen und Lösungen. *Helv. Chim. Acta*, **28**, 97–127 (1945)
254. Kunst, M. and J. M. Warman: Nanosecond time-resolved conductivity studies of pulse-ionized ice. 2.The mobility and trapping of protons. *J. Chem. Phys.*, **87**, 4093–4095 (1983)
255. Kuzuu, N. and M. Doi: Constitutive equation for nematic liquid liquid crystals under weak velocity gradient derived from a molecular kinetic equation. *J. Phys. Soc. Japan*, **52**, 3486–3494 (1983)
256. Lakoff, G. and R. E. Núñez: *Where Mathematics Comes From*. Basic Books, New York (2000)
257. Larson, R. G.: *Constitutive Equations for Polymer Melts and Solutions*. Butterworths, Boston (1988)
258. Lätzel, M.; S. Luding and H. J. Herrmann: Macroscopic material properties from quasi-static, microscopic simulations of a two-dimensional shear-cell. *Granular Matter*, **2**, 123–135 (2000)
259. Lätzel, M.; S. Luding and H. J. Herrmann: From discontinuous models towards a continuum description. In: *Continuous and Discontinuous Modelling of Cohesive-Frictional Materials*, edited by P. Vermeer; S. Diebels; W. Ehlers; H. J. Herrmann; S. Luding and E. Ramm, pp. 215–229. Springer, Berlin (2001)
260. Leal, L. G. and E. J. Hinch: The effect of weak Brownian rotations on particles in shear flow. *J. Fluid Mech.*, **46**, 685–703 (1971)
261. Leal, L. G. and E. J. Hinch: Theoretical studies of a suspension of rigid particles affected by Brownian couples. *Rheol. Acta*, **12**, 127–132 (1973)
262. Lebensohn, R. A. and C. N. Tomé: A self-consistent anisotropic approach for the simulaton of plastic deformation and texture development of polycrystals: application to zirconium alloys. *Acta Metall.*, **41**, 2611–2624 (1993)
263. Lehner, D.; H. Lindner and O. Glatter: Determination of the translational and rotational diffusion coefficients of rodlike particles using depolarized dynamic light scattering. *Langmuir*, **16**, 1689–1695 (2000)
264. Leslie, F. M.: The stability of Couette flow of certain anisotropic fluids. *Proc. Cambridge Philos. Soc.*, **60**, 949–955 (1964)
265. Leslie, F. M.: Constitutive equations for anisotropic fluids. *Q. J. Mech. Appl. Math.*, **19**, 357–370 (1966)
266. Leslie, F. M.: Some constitutive equations for liquid crystals. *Arch. Rational Mech. Anal.*, **28**, 265–283 (1968)
267. Leslie, F. M.: Some thermal effects in cholesteric liquid crystals. *Proc. Roy. Soc. A*, **307**, 359–372 (1968)
268. Leslie, F. M.: On the thermodynamics of polar fluids. *Arch. Rational Mech. Anal.*, **70**, 189–202 (1979)
269. Leslie, F. M.: Thermo-mechanical effects in cholesteric liquid crystals. *J. Non-Eq. Thermodyn.*, **11**, 23–24 (1985)
270. Leslie, F. M.: Continuum theory of nematic liquid crystals. *Continuum Mech. Thermodyn.*, **4**, 167–175 (1992)
271. Lewis, G. N. and M. Randall: *Thermodynamics*. 2nd edn. McGraw-Hill, New York (1961). Revised by K. S. Pitzer and L. Brewer
272. Libbrecht, K. G.: A cylindrically symmetric Green's function approach for modelling the crystal growth morphology of ice. *Phys. Rev. E*, **60**, 1967–1974 (1999)
273. Lipenkov, V. Y.; N. I. Barkov; P. Duval and P. Pimienta: Crystalline texture of the 2083m ice core at Vostok Station, Antarctica. *J. Glaciol.*, **35**, 392–398 (1989)
274. Liu, I.-S.: Method of Lagrange multipliers for exploitation of the entropy. *Arch. Rat. Mech. Anal.*, **46**, 131–148 (1972)
275. Liu, I.-S.: *Continuum Mechanics*. Springer, New York (2002)
276. Lliboutry, L.: *Very Slow Flows of Solids*. Kluwer, Dordrecht (1987)
277. Lliboutry, L.: Anisotropic, transversely isotropic nonlinear viscosity of rock ice and rheological parameters inferred from homogenization. *J. Plast.*, **9**, 619–632 (1993)
278. Lliboutry, L. and P. Duval: Various isotropic and anisotropic ices found in glaciers and polar ice caps and their corresponding rheologies. *Ann. Geophysicae*, **3**, 207–224 (1985)
279. Lobban, C.; J. L. Finney and W. F. Kuhs: The structure of a new phase of ice. *Nature*, **391**, 268–270 (1998)
280. Lodge, A. S.: *Elastic Liquids*. Academic Press, London (1964)
281. Love, A. E. H.: *A Treatise on the Mathematical Theory of Elasticity*. 4th edn. Dover, New York (1944). Originally published by Cambridge University Press, Cambridge, 1927

282. Lubachevsky, B. D.: How to simulate billiards and similar systems. *J. Comput. Physics*, **94**, 255–283 (1991)
283. Lucretius Carus, T.: *On the Nature of Things*. Hackett, New York (2001). Translated by Martin Ferguson Smith
284. Luding, S.: Stress distribution in static two dimensional granular model media in the absence of friction. *Phys. Rev. E*, **55**, 4720–4729 (1997)
285. Luding, S.; J. Duran; E. Clément and J. Rajchenbach: Simulations of dense granular flow: dynamic arches and spin organization. *J. Phys. I*, **6(6)**, 823–836 (1996)
286. Lun, C. K. K.; S. B. Savage; D. J. Jeffrey and N. Chepurniy: Kinetic theories of granular flow: inelastic particles in Couette flow and slightly inelastic particles in a general flowfield. *J. Fluid Mech.*, **140**, 223–256 (1984)
287. MacMillan, E. H.: Slow flows of anisotropic fluids. *J. Rheol.*, **33**, 1071–1105 (1989)
288. Madeleine-Perdrillat, A.: Seurat: a ciência do pintor. In: *Artepensamento*, edited by A. Novaes, pp. 287–297. Companhia das Letras, São Paulo (1994)
289. Mansuy, P.; A. Philip and J. Meyssonnier: Identification of strain heterogeneities arising during deformation of ice. *Ann. Glaciol.*, **30**, 121–126 (2000)
290. Marsden, J. E. and T. J. R. Hughes: *Mathematical Foundations of Elasticity*. 2nd edn. Prentice-Hall, Englewood Cliffs (1983)
291. Martins-Costa, M. L. and R. M. Saldanha da Gama: Consitutive relations for the energy transfer in nonsaturated continuous mixtures. *Mech. Research Comm.*, **23(2)**, 117–122 (1996)
292. Mason, B. J.; G. W. Bryant and A. P. van den Heuvel: The growth habits and surface structure of ice crystals. *Philos. Mag.*, **8**, 505–526 (1963)
293. Maugin, G. A. and R. Drouot: Internal variables and the thermodynamics of macromolecule solutions. *Int. J. Engng. Sci.*, **21**, 705–724 (1983)
294. Maxwell, J. C.: Experiments on colour as perceived by the eye, with remarks on colour-blindness. *Trans. Roy. Soc. Edinburgh*, **21**, 275–298 (1855)
295. Maxwell, J. C.: On the theory of compound colours, and the relations of the colours of the spectrum. *Philos. Trans.*, **150**, 57–84 (1860)
296. Maxwell, J. C.: On the dynamical theory of gases. *Phil. Trans. Royal Soc. London A*, **157**, 49–88 (1867)
297. Maxwell, J. C.: *A Treatise on Electricity and Magnetism*, vol. 2 of *Clarendon Press Series*. Oxford University Press, Oxford (1873)
298. Maxwell, J. C.: Letter to Peter Guthrie Tait, 7 November 1970. In: *The Scientific Letters and Papers of James Clerk Maxwell*, edited by P. M. Harman, vol. II, pp. 568–569. Cambridge University Press, Cambridge (1990). Original in the University Library, Cambridge
299. Maxwell, J. C.: Notes on space and position, circa 1857. In: *The Scientific Letters and Papers of James Clerk Maxwell*, edited by P. M. Harman, vol. I, pp. 515–516. Cambridge University Press, Cambridge (1990). Original in the University Library, Cambridge
300. McComb, W. D.: *The Physics of Fluid Turbulance*. Oxford Engineering Science Series, 25, 1st edn. Oxford University Press, Oxford (1990)
301. McConnel, J. C.: On the plasticity of an ice crystal. *Proc. Roy. Soc. London*, **49**, 323–343 (1891)
302. Mehrabadi, M. M.; S. Nemat-Nasser and M. Oda: On statistical description of stress and fabric in granular materials. *Int. J. Numer. Anal. Methods Geomech.*, **6**, 95–108 (1982)
303. Merrington, A. C.: Flow of visco-elastic materials in capillaries. *Nature*, **152**, 663 (1943)
304. Meyssonnier, J. and A. Philip: A model for the tangent viscous behaviour of anisotropic polar ice. *Ann. Glaciol.*, **23**, 253–261 (1996)
305. Meyssonnier, J. and A. Philip: Comparison of finite-element and homogenization methods for modelling the viscoplastic behaviour of a S2-columnar-ice polycrystal. *Ann. Glaciol.*, **30**, 115–120 (2000)
306. Mishima, O. and H. E. Stanley: The relationship between liquid, supercooled and glassy water. *Nature*, **396**, 329–335 (1998)
307. Moelwyn-Hughes, E. A.: Der osmotische Druck. *Z. Elektrochem.*, **55(6)**, 518–525 (1951)
308. Montagnat, M. and P. Duval: Rate controlling processes in the creep of polar ice, influence of grain boundary migration associated with recrystallization. *Earth Planet. Sci. Lett.*, **183**, 179–186 (2000)
309. Morland, L. W.: A simple constitutive theory for a fluid-saturated porous solid. *J. Geophys. Res.*, **77(5)**, 890–900 (1972)
310. Morland, L. W. and S. Sellers: Multiphase mixtures and singular surfaces. *Int. J. Non-Lin. Mech.*, **36**, 131–146 (2001)
311. Morland, L. W. and R. Staroszczyk: Viscous response of polar ice with evolving fabric. *Continuum Mech. Thermodyn.*, **10**, 135–152 (1998)
312. Moura Neto, F.; P. J. Paes Leme; H. P. Amaral Souto and A. S. Vargas: Inertial and second grade effects on macroscopic equations for the flow of a fluid in a porous medium. *Transport in Porous Media*, **33**, 205–226 (1998)
313. Mühlhaus, H.-B.; H. Sakagushi and L. Moresi: Discrete and continuum modelling of granular materials. In: *Constitutive Modelling of Granular Materials*, edited by D. Kolymbas, pp. 209–224. Springer, Berlin (2000)

314. Mühlhaus, H.-B. and I. Vardoulakis: The thickness of shear bands in granular materials. *Géotechnique*, **37**, 271–283 (1987)
315. Müller, I.: A thermodynamic theory of mixtures of fluids. *Arch. Rat. Mech. Anal.*, **28**, 1–39 (1968)
316. Müller, I.: Thermodynamics of mixtures of fluids. *J. Mécanique*, **14**, 267–303 (1975)
317. Müller, I.: *Thermodynamics*. Pitman, London (1985)
318. Müller, I.: Integration and segregation in a population - a thermodynamicists's view. In: *Continuum Mechanics and Applications in Geophysics and the Environment*, edited by B. Straughan; R. Greve; H. and Y. Wang, pp. 44–55. Springer, Heidelberg (2001)
319. Müller, I.: In memoriam Frank Matthews Leslie, F.R.S. *Continuum Mech. Thermodyn.*, **14**, 227–229 (2002)
320. Murray, J. D.: *Mathematical Biology*. 2nd edn. Springer, Berlin (1993)
321. Needham, J. and L. Gwei-Djen: The earliest snow crystal observations. *Weather*, **16**, 319–327 (1961)
322. Nicolis, G. and I. Prigogine: *Self-organization in Nonequilibrium Systems*. Wiley, New York (1977)
323. Nield, V. M. and R. W. Whitworth: The structure of ice Ih from analysis of single-crystal neutron diffuse scattering. *J. Phys. Condens. Matter.*, **7**, 8259–8271 (1995)
324. Noll, W.: On the continuity of the solid and fluid states. *J. Rat. Mech. Anal.*, **4**, 3–81 (1955)
325. Norton, F. H.: *The Creep of Steel at High Temperatures*. McGraw-Hill, New York (1929)
326. Nunziato, J. W. and E. K. Walsh: On ideal multiphase mixtures with chemical reactions and diffusion. *Arch. Rat. Mech. Anal.*, **73**, 285–311 (1980)
327. Nye, J. F.: The flow law of ice from measurements in glacier tunnels laboratory experiments and the Jungfraufirn experiment. *Proc. Roy. Soc. London A*, **219**, 477–489 (1953)
328. Nye, J. F.: The distribution of stress and velocities in glaciers and ice-sheets. *Proc. Roy. Soc. London A*, **239**, 113–133 (1957)
329. Oda, M. and K. Iwashita: Study on couple stress and shear band development in granular media based on numerical simmulation analyses. *Int. J. Engng. Sci.*, **38**, 1713–1740 (2000)
330. Odell, J. A.; A. Keller and E. D. T. Atkins: Diffusion and orientability of rigid-rodlike molecules in solution. *Macromolecules*, **18**, 1443–1453 (1985)
331. Odqvist, F. K. G.: Historical survey of the development of creep mechanics from its beginnings in the last century to 1970. In: *Creep in Structures (IUTAM-Symposium)*, edited by A. R. S. Ponter and D. R. Hayhurst, pp. 1–12. Springer, Berlin (1981)
332. Okino, M. S. and M. L. Mavrovouniotis: Simplification of mathematical models of chemical reaction sytems. *Chem. Rev.*, **98(2)**, 391–408 (1998)
333. Okubo, A.: *Diffusion and Ecological Problems: Mathematical Models*. Springer, Berlin (1980)
334. Orowan, E.: Problems of plastic gliding. *Proc. Phys. Soc.*, **52**, 8–22 (1940)
335. Oseen, C. W.: Beiträge zur Theorie der anisotropen Flüssigkeiten. *Ark. Mat. Astron. Fys.*, **19a**, 1–18 (1925)
336. Ostwald, W.: Über die Geschwindigkeitsfunktion der Viskosität disperser Systeme. I. *Kolloid-Z.*, **36**, 99–117, 157–333, 248–250 (1925)
337. Pan, Y. and R. N. Horne: Generalized macroscopic models for fluid flow in deformable porous media I: theories. *Transport in Porous Media*, **45**, 1–27 (2001)
338. Panfilov, M.: *Macroscale Models of Flow Through Highly Heterogeneous Porous Media*. Theory and Applications of Transport in Porous Media, 16. Kluwer, Dordrecht (2000)
339. Panofsky, W. K. H. and M. Phillips: *Classical Electricity and Magnetism*. 2nd edn. Addison-Wesley, Reading (1962)
340. Pao, Y.-H.: Hydrodynamic theory for the flow of a viscoelastic fluid. *J. Appl. Phys.*, **28**, 591–598 (1957)
341. Pao, Y. H. and K. Hutter: Electrodynamics of moving elastic solids and viscous fluids. *Proc. IEEE*, **63**, 1011–1021 (1975)
342. Paterson, W. S. B.: Why ice-age is sometimes "soft". *Cold Reg. Sci. Technol.*, **20**, 75–98 (1991)
343. Paterson, W. S. B.: *The Physics of Glaciers*. 3rd edn. Pergamon, Oxford (1994)
344. Pauling, L.: The structure and entropy of ice and of other crystals with some randomness of atomic arrangement. *J. Amer. Chem. Soc.*, **57**, 2680–2684 (1935)
345. Peixoto, F. C.; G. M. Platt and F. L. P. Pessôa: Vapor-liquid equilibria of multi-indexed continuous mixtures using an equation of state and group contribution methods. *Chem. Engng. J.*, **77**, 179–187 (2000)
346. Peltier, W. R.; D. L. Goldsby and L. Tarasov: Ice-age ice-sheet rheology: constraints from the Last Glacial Maximum form of the Laurentide ice sheet. *Ann. Glaciol.*, **30**, 163–176 (2000)
347. Peterlin, A.: Über die Viskosität von verdünnten Lösungen und Suspensionen in Abhängigkeit von der Teilchenform. *Z. Phys.*, **111**, 232–263 (1938)
348. Peterlin, A. and H. A. Stuart: Über die Bestimmung der Größe und Form, sowie der elektrischen, optischen und magnetischen Anisotropie von submikroskopische Teilchen mit Hilfe der künstlichen Doppelbrechung und der inneren Reibung. *Z. Phys.*, **112**, 129–147 (1939)
349. Peterlin, A. and H. A. Stuart: Zur Theorie der Strömungsdoppelbrechung von Kolloiden und großen Molekülen in Lösung. *Z. Phys.*, **112**, 1–19 (1939)
350. Petrie, C. J. S.: The rheology of fibre suspensions. *J. Non-Newton. Fluid Mech.*, **87**, 369–402 (1999)
351. Poirier, J.-P.: *Creep of Crystals*. Cambridge University Press, Cambridge (1985)

352. Pop, J. J. and R. M. Bowen: A theory of mixtures with a long range spatial interaction. *Acta Mechanica*, **29**, 21–34 (1978)
353. Post, A. and E. R. LaChapelle: *Glacier Ice*. University of Washington Press and the International Glaciological Society, Seattle and Cambridge (2000)
354. Prager, S.: Interaction of rotational and translational diffusion. *J. Chem. Phys.*, **23**, 2404–2407 (1955)
355. Prager, S.: Stress-strain relations in a suspension of dumbbells. *Trans. Soc. Rheol.*, **1**, 53–62 (1957)
356. Prigogine, I.: Modération et transformations irréversibles des systèmes ouverts. *Bull. Cl. Sci., Acad. R. Belg.*, **31**, 600–606 (1945)
357. Radjai, F.; M. Jean; J.-J. Moreau and S. Roux: Force distributions in dense two-dimensional granular systems. *Physical Review Letters*, **77(2)**, 274–277 (1996)
358. Radjai, F. and D. E. Wolf: Features of static pressure in dense granular media. *Granular Matter*, **1**, 3–8 (1998)
359. Radjai, F.; D. E. Wolf; J. Michel and J.-J. Moreau: Bimodal character of stress transmission in granular packings. *Physical Review Letters*, **80(1)**, 61–64 (1998)
360. Reeh, N.: Dating by ice flow modelling: a useful tool or an exercise in applied mathematics? In: *The Environmental Record in Glaciers and Ice Sheets*, edited by H. Oeschger and C. C. Langway, Jr., pp. 141–159. Wiley, Chichester (1989)
361. Reuss, A.: Berechnung der FlieSSgrenze von Mischkristallen auf Grund der Plastizitätsbedingung für Einkristalle. *Z. Angw. Math. Mech.*, **9**, 49–58 (1929)
362. Rinne, F.: Das Kristallsystem und das Achsenverhältnis des Eises. *Ber. Verh. Sächs. Acad. Wiss., Math.-Phys.*, **69**, 57–62 (1917)
363. Riseman, J. and J. G. Kirkwood: The intrinsic viscosity, translational and rotatory diffusion constants of rod-like macromolecules in solution. *J. Chem. Phys.*, **18**, 512–516 (1950)
364. Risken, H.: *The Fokker–Planck Equation*. 2nd. edn. Springer, Berlin (1996)
365. Rossmann, F.: *Johannes Kepler – Neujahrsgabe oder Vom sechseckigen Schnee*. Keiper, Berlin (1943)
366. Sachs, G.: Zur Ableitung einer FlieSSbedingung. *Z. Ver. Deutscher Ing.*, **72**, 734–736 (1928)
367. Sage, B. H.: *Thermodynamics of Multicomponent Systems*. Reinhold, New York (1965)
368. Saldanha da Gama, R. M. and M. L. Martins-Costa: Incompressible fluid flow and heat transfer through a nonsaturated porous medium. *Computational Mechanics*, **20**, 479–494 (1997)
369. Sammonds, P. R.: Understanding the fundamental physics governing the evolution and dynamics of the Earth's crust and ice sheets. *Phil. Trans. Roy. Soc. London A*, **357**, 3377–3401 (1999)
370. Sampaio, R. and W. O. Williams: Thermodynamics of diffusing mixtures. *J. Mécanique*, **18**, 19–45 (1979)
371. Savage, S. B. and K. Hutter: The motion of a finite mass of granular material down a rough incline. *J. Fluid Mech.*, **199**, 177–215 (1989)
372. Savage, S. B. and C. K. K. Lun: Particle size segregation in inclined chute flow of dry cohesionless granular solids. *J. Fluid Mech.*, **189**, 311–335 (1988)
373. Schapiro, M.: Seurat. In: *Modern Art: 19th & 20th Centuries*, vol. 2 of *Selected Papers*, pp. 101–109. Brazillier, New York (1978)
374. Scheel, H. J.: Historical introduction. In: *Handbook of Crystal Growth*, edited by D. T. J. Hurle, pp. 1–42. Elsevier, Amsterdam (1993)
375. Schmid, E. and W. Boas: *Kristallplastizität*. Springer, Berlin (1935)
376. Schulson, E. M.: The structure and mechanical behavior of ice. *JOM*, **51**, 21–27 (1999)
377. Senechal, M.: Brief history of geometrical crystallography. In: *Historical Atlas of Crystallography*, edited by J. Lima-de Faria, pp. 43–60. Kluwer, Dordrecht (1990)
378. Shelley, M.: *Frankenstein*. The Golden Heritage Series. Galley Press, Leicester (1988)
379. Siegert, M. J.: *Ice Sheets and Late Quaternary Environmental Change*. John Wiley & Sons, Chichester (2001)
380. Smith, G. F.: On isotropic functions of symmetric tensors, skew-symmetric tensors and vectors. *Int. J. Engng. Sci.*, **9**, 899–916 (1971)
381. Spencer, A. J. M.: Theory of invariants. In: *Continuum Physics*, edited by A. C. Eringen, vol. I, pp. 239–353. Academic Press, New York (1971)
382. St. John, A.: The crystal structure of ice. *Proc. Nat. Acad. Sci. Amer.*, **4**, 193–196 (1918)
383. Staroszczyk, R.: An orthotropic constitutive model for secondary creep of ice. *Arch. Mech.*, **53**, 65–85 (2001)
384. Staroszczyk, R. and O. Gagliardini: Two orthotropic models for strain-induced anisotropy of polar ice. *J. Glaciol.*, **45**, 485–494 (1999)
385. Staroszczyk, R. and L. W. Morland: Orthotropic viscous response of polar ice. *J. Engng. Math.*, **37**, 191–209 (2000)
386. Staroszczyk, R. and L. W. Morland: Plane ice-sheet flow with evolving orthotropic fabric. *Ann. Glaciol.*, **30**, 93–101 (2000)
387. Staroszczyk, R. and L. W. Morland: Strengthening and weakening of induced anisotropy in polar ice. *Proc. Roy. Soc. London A*, **451(2014)**, 2419–2440 (2001)
388. Staroszczyk, R. and M. L. W.: Orthotropic viscous model for ice. In: *Advances in Cold-Region Thermal Engineering and Sciences*, edited by K. Hutter; Y. Wang and H. Beer, pp. 249–258. Springer, Berlin (1999)

389. Starr, C. G.: *A History of the Ancient World*. 4th edn. Oxford University Press, Oxford (1991)
390. Stefan, J.: Über das Gleichgewicht und die Bewegung, insbesondere die Diffusion von Gasmengen. *Sitzungsber. Akad. Wiss. (Wien), Math.-Naturwiss. Kl., Abt.II*, **63**, 63–124 (1871)
391. Steinemann, S.: Results of preliminary experiments on the plasticity of ice crystals. *J. Glaciol.*, **2**, 404–412 (1954)
392. Steinemann, S.: *Experimentelle Untersuchungen zur Plastizität von Eis*. Ph.d. thesis, Eidgenössischen Technischen Hochschule (ETH), Zürich (1958)
393. Stephen, M. J. and J. P. Straley: Physics of liquid crystals. *Rev. Mod. Phys.*, **46(4)**, 617–704 (1974)
394. Svendsen, B. and K. Hutter: On the thermodynamics of a mixture of isotropic materials with constraints. *Int. J. Engng. Sci.*, **33**, 2021–2054 (1995)
395. Svendsen, B. and K. Hutter: A continuum approach for modelling induced anisotropy in glaciers and ice sheets. *Ann. Glaciol.*, **23**, 262–269 (1996)
396. Tai, Y.-C.; Y. Wang; J. M. N. T. Gray and K. Hutter: Methods of similitude in granular avalanche flows. In: *Advances in Cold-Region Thermal Engineering and Sciences: Technological, Environmental and Climatological Impact*, edited by K. Hutter; Y. Wang and H. Beer, Lecture Notes in Physics 533, pp. 416–428. Springer, Berlin (1999)
397. Tait, P. G.: *An Elementary Teatise on Quaternions*. 3rd edn. Cambridge University Press, Cambridge (1890)
398. Takahashi, T.: Debris flow. *Ann. Rev. Fluid Mech.*, **13**, 57–77 (1981)
399. Taylor, G. I.: Plastic strain in metals. *J. Inst. Metals*, **62**, 307–324 (1938)
400. Terzaghi, K.: *Erdbaumechanik auf bodenphysikalischer Grundlage*. Deuticke, Leipzig (1925)
401. Terzaghi, K.: *Theoretical Soil Mechanics*. John Wiley and Sons, Inc., New York (1948)
402. Thorsteinsson, T.: Textures and fabrics in the GRIP ice core, in relation to climate history and ice deformation. Berichte zur polarforschung, Alfred-Wegener-Institut für Polar- und Meeresforschung, Bremerhaven (1996)
403. Thorsteinsson, T.; E. D. Waddington; K. C. Taylor; R. B. Alley and D. D. Blankenship: Strain-rate enhancement at Dye 3, Greenland. *J. Glaciol.*, **45**, 338–345 (1999)
404. Truesdell, C.: Hypo-elasticity. *J. Rat. Mech. Anal.*, **4**, 83–133, 1019–1020 (1955)
405. Truesdell, C.: Sulle basi della termomeccanica. *Rend. Fis. Acc. Lincei Series VIII*, **22**, 33–38, 158–166 (1957)
406. Truesdell, C.: *Six Lectures on Modern Natural Philosophy*. Springer, Berlin (1966)
407. Truesdell, C.: *Rational Thermodynamics*. 2nd edn. Springer, New York (1984)
408. Truesdell, C. and W. Noll: The nonlinear field theories of mechanics. In: *Handbuch der Physik*, edited by S. Flügge, vol. III/3, p. 602. Springer, Berlin (1965)
409. Truesdell, C. and R. Toupin: The classical field theories. In: *Handbuch der Physik*, edited by S. Flügge, vol. III/1, pp. 226–793. Springer, Berlin (1960)
410. Turing, A. M.: The chemical basis of morphogenesis. *Phil. Trans. Roy. Soc. London B*, **237**, 37–72 (1952)
411. Twiss, R. J. and A. C. Eringen: Theory of mixtures for Micromorphic materials - I: balance laws. *Int. J. Engng. Sci.*, **9**, 1019–1044 (1971)
412. Van der Veen, C. J.: *Fundamentals of Glacier Dynamics*. Balkema, Rotterdam (1999)
413. Van der Veen, C. J. and I. M. Whillans: Flow laws for glacier ice: comparison of numerical predictions and field measurements. *J. Glaciol.*, **36**, 324–339 (1990)
414. Van der Veen, C. J. and I. M. Whillans: Development of fabric in ice. *Cold Reg. Sci. Technol.*, **22**, 171–195 (1994)
415. Van Houtte, P.: On the equivalence of the relaxed Taylor theory and the Bishop and Hill theory for partially constrained plastic deformation of crystals. *J. Matter. Sci. Engng.*, **55**, 69–77 (1982)
416. Voigt, W.: Theoretische Studien über die Elasticitätsverhältnisse der Krystalle. *Abh. Königl. Ges. Wiss. Göttingen*, **34**, 3–100 (1887)
417. Voigt, W.: *Kompendium der Theoretischen Physik*, vol. 1. Von Veit, Leipzig (1895)
418. Volterra, V.: Sopra le funzioni che dipendono da altre funzioni. *R. Acc. Lincei Rend.*, **3**, 97–105, 141–146, 153–158 (1887)
419. Von Mises, R.: Mechanik der plastischen Formänderung von Kristallen. *Z. Angew. Math. Mech.*, **8**, 161–185 (1928)
420. Wakahama, G.: On the plastic deformation of ice. *Low Temp. Sci. A*, **20**, 57–130 (1962)
421. Wang, C.-C.: A new representation theorem for isotropic functions. Part I. *Arch. Rational Mech. Anal.*, **36**, 166–197, 198–223 (1970). Corrigendum ibid. 43, 392–395 (1971)
422. Weertman, J.: Creep deformation of ice. *Ann. Rev. Earth Planet Sci.*, **11**, 215–240 (1983)
423. Weissenberg, K.: A continuum theory of rheological phenomena. *Nature*, **159**, 310–311 (1947)
424. Weissenberg, K.: Abnormal substances and abnormal phenomena of flow. In: *Proceedings of the International Congress of Rheology, Scheweningen, 1948*, vol. I. North Holland, Amsterdam (1949)
425. Weissenberg, K.: Specification of rheological phenomena by means of a rheogoniometer. In: *Proceedings of the International Congress of Rheology, Scheweningen, 1948*, vol. II. North Holland, Amsterdam (1949)
426. Weyl, H.: *Das Kontinuum*. Veit, Leipzig (1918)
427. Whitaker, S.: Diffusion and dispersion in porous media. *A.I.Ch.E. J.*, **13(3)**, 420–427 (1967)

428. Whittaker, E. T.: Vito Volterra. *Obituary Notices of Fellows of the Roy. Soc. London*, **3**, 619–729 (1941)
429. Whitworth, R. W.: The influence of the choice of glide plane on the theory of the velocity of dislocations in ice. *Philos. Mag.*, **41**, 521–528 (1980)
430. Whitworth, R. W.; J. G. Paren and J. W. Glen: The velocity of dislocations in ice - a theory based on proton disorder. *Philos. Mag.*, **33**, 409–426 (1976)
431. Whyte, L. L.; C. Hardie and B. J. Mason: *Johannes Kepler: The Six-Cornered Snowflake*. Clarendon, Oxford (1966)
432. Wilchinsky, A. V.; S. H. Faria and K. Hutter: Thermodynamic modelling of polymer solutions with molecular form birefringence. *J. Non-Newton. Fluid Mech.*, **99**, 57–77 (2001)
433. Wilmański, K.: *Thermomechanics of Continua*. Springer, Berlin (1998)
434. Wilson, C. J. L. and Y. Zhang: Development of microstructure in the high-temperature deformation of ice. *Ann. Glaciol.*, **23**, 293–302 (1996)
435. Wittstein, G. C.: *Plinnius- Die Naturgeschichte*, vol. 6. Gressner& Schramm, Leipzig (1882)
436. Wollaston, W. H.: On the elementary particles of certain crystals. *Phil. Trans. Roy. Soc. London*, pp. 51–63 (1813)
437. Zero, K. M. and R. Pecora: Rotational and translational diffusion in semidilute solutions of rigid-rod macromolecules. *Macromolecules*, **15**, 87–93 (1982)

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